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UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

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MANGANESE; ITS OCCURRENCE, MILLING, AND METALLURGY

PART III.

CHAPTER 6. GENERAL METALLURGY OF MANGANESE

CHAPTER 7. HYDROMETALLURGY OF MANGANESE

CHAPTER 8. PYROMETALLURGICAL TREATMENT OF MANGANESE ORES

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R. S. DEAN, EDMUND S. LEAVER, AND T. L. JOSEPH

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UNITED STATES BUREAU OF MINES

MANGANESE; ITS OCCURRENCE, MINING, AND METALLURGY[1]

PART III

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CHAPTER 6. GENERAL METALLURGY OF MANGANESE

By R. S. Dean[2]

The metallurgy of manganese has developed along the lines of iron metallurgy. Enough high-grade ore has been available so that by reduction with carbon it could be turned into an iron-manganese alloy and a slag containing some 9 to 15 percent manganese. More siliceous ores have been smelted in the blast furnace to form iron-silicon-manganese alloys called spiegel.

When lower-grade ores came in for serious consideration, which has only been since 1914, two types of processes received the most consideration -- hydrometallurgical processes to produce a concentrate which could be smelted like the higher-grade ore and processes involving concentration of the manganese from manganiferous iron ores by preferential reduction of the iron (184)[3].

Special chapters in this bulletin are devoted to the production of ferromanganese from ore, the hydrometallurgy of manganese, and the Bureau of Mines modification of the preferential reduction process.

Other methods of producing manganese alloys from low-grade or refractory ores have been suggested and may find future application.

Manganese has a very high affinity for sulphur and is particularly adaptable to concentration by matte smelting. According to Betts (26), manganese silicate may be smelted with pyrite to give manganese sulphide and iron silicate. This method would be applicable to concentration of either the silicate or carbonate ores. The sulphide, once obtained, could be roasted to oxide and reduced in the usual way.

Another possibility for the production of manganese from silicate ores involves their reduction by silicon or manganese silicides. Swedish Patent 58290, February 25, 1925, covers the reduction of a slag rich in manganese by silicon-manganese alloy containing more than 10 percent silicon, Joseph H. Brennan (38) describes the concentration of manganese iron ores by partial reduction with silicon. Beckett (3,4,19) describes the reduction of manganese dioxide with a manganese silicide for the production of standard ferromanganese. Beckett gives as a typical alloy, manganese 64.4, silicon 24.6, and as a typical ore, 56.50 manganese as MnO_2. The product of the reaction between these two is 80.11 percent manganese and 1.22 percent silicon.

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2 Chief engineer, Metallurgical Division, U.S. Bureau of Mines.

3 Throughout parts I to IV, numbers in parentheses refer to items in this bibliography, and page numbers to those in the reference cited.

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CHAPTER 7. HYDROMETALLURGY OF MANGANESE

By Edmund S. Leaver[4]

Hydrometallurgical methods for utilization of low-grade deposits of manganese ore present a difficult problem in comparison with the usual leaching processes for the recovery of precious metals or even with the process of leaching a 1-percent copper ore. In the concentration of manganese ore by lixiviation methods the solvent must be cheap or through regeneration become available for reuse at low cost. This is easily understood when we consider that the average milling grade of manganese ore will exceed 15 percent in manganese content and will require a corresponding amount of chemical in the solvent solution to react with it to effect dissolution necessary for separation and removal from the ore residue. Other problems are the recovery of the manganese from the solvent solution and the regeneration of the chemicals used. The feasibility of treating manganese ores by hydrometallurgical processes is, of course, governed by the cost of treatment and the selling price of the manganese product. The high cost of dissolving the manganese mineral and the ease with which the solutions can be purified favor the preparation of a high-grade product. Such products include the manganese compounds that enter into the textile industry and the manufacture of electric batteries, glass, pottery, tile, brick, paint, ink, and fertilizers.

LARGE MANGANESE DEPOSITS IN THE UNITED STATES

The principal large bodies of manganese ores known to be available in the United States and thought to be probable sources of supply for some form of hydrometallurgical treatment are listed in table 65.

More details on the occurrence of each of these manganese deposits, including physical properties and results of concentration experiments, are given in chapter 4.

TYPES OF ORES

From a hydrometallurgical standpoint manganese ores may be divided into several types: (1) Ores in which the manganese mineral is readily soluble in at least one solvent; (2) ores in which the manganese mineral requires preliminary treatment to make it soluble; (3) ores containing manganese in insoluble form; (4) ores which destroy excessive amounts of solvents due to soluble impurities; (5) ores which present physical properties that increase the cost of treatment.

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4 Metallurgist, U. S. Bureau of Mines.

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TABLE 65. - Large Manganese Deposits in the United States

(Possible source for hydrometallurgical treatment)

Name and location	Tonnage	Type of ore	Mineral
Kingman district, Ariz.	50,000,000	Oxides in sandstone and shale.	Psilomelane, quartz, calcite, gypsum, feldspar.
Batesville, Ark.	420,000	Ferruginous clay and shale.	Psilomelane and braunite iron oxides.
Leadville, Colo.	3,000,000	Ferruginous in limestone.	Oxides of manganese and iron.
Cartersville district, Ga.	5,000,000	Clay and quartzite.	Psilomelane.
Cuyuna, Minn.	30,000,000	Finely disseminated ferruginous, siliceous chert.	Psilomelane hematite.
Butte, Mont.	400,000 (1)	Siliceous oxides. Siliceous carbonate.	Pyrolusite. Rhodochrosite.
Philipsburg, Mont.	1,780,000	Quartz gangue.	Pyrolusite and other oxides.
Las Vegas, Nev.	285,000	Clay and tuff.	Wad and pyrolusite.
Little Florida Mountains, N.Mex.	700,000	Felsitic rhyolite.	Wad; pyrolusite and psilomelane.
Silver City, N. Mex.	1,000,000	Dolomite lime.	Pyrolusite, manganite, and hematite.
Chamberlain, S. Dak.	100,000,000	Shale with nodules of ----	Carbonates of manganese iron, lime.
Blue Ridge, Va.	1,000,000	Siliceous clay.	Psilomelane.

1/ Very large.

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TABLE 65. - Large Manganese Deposits in the United States--Continued

Name and location	Analysis, percent				Remarks
	Mn	Fe	P	SiO_2	
Kingman district, Ariz.	8.1	2.3	0.05	68.5	Flotation not satisfactory; gravity concentration poor.
Batesville, Ark.	6.6	7.5	.30	33.3	Flotation no hope; gravity not successful.
Leadville, Colo.	19.6	20.4	.04	7.41	Better grade, shipped to Pueblo.
Cartersville district, Ga.	31.2	16.8	.16	10.2	Concentrating and shipping the better grade ore.
Cuyuna, Minn.	15.0	29.5	.03	25.2	Concentration difficult.
Butte, Mont.	12.3	2.4	.04	75.0	Flotation negative.
Philipsburg, Mont.	21.3 18.0	2.64 3.1	.18	49.4 58.4	Flotation good. Concentrated with big loss in tails, used battery for crushing.
Las Vegas, Nev.	24.0	2.0	.05	35.0	Difficult to concentrate.
Little Florida Mountains, N.Mex.	22.6	2.7	.14	39.2	Concentrate and ship.
Silver City, N. Mex.	13.0	39.0	.01	8.0	Does not concentrate favorably.
Chamberlain, S. Dak.	16.0	11.0	.44	13.0	Analysis is for nodules.
Blue Ridge, Va.	35.0	3.5	- -	12.0	Concentrated by jigs and tables.

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In class 1 belong all the higher oxides of manganese, such as pyrolusite, psilomelane, braunite, and wad. These minerals are readily soluble in acids but require a reducing roast to prepare them for ammonia leaching. In class 2 belongs rhodochrosite, which requires roasting to expel carbon dioxide before the manganese is readily soluble in sulphurous acid or ammonia. To class 3 belong rhodonite and the partly oxidized black silicate, which are practically insoluble in the usual leaching circuits. Class 4 is represented by ores with high-lime gangue, which precludes acid leaching and favors an alkaline circuit. In class 5 fall ores that contain clay or talc, are more difficult to leach, and are usually benefited by roasting.

DISSOLUTION OF MANGANESE MINERALS IN SULPHUROUS ACID

Although the literature reveals a large number of solvents which have been prepared for determination of manganese minerals, the rate of solution of various minerals has been investigated in only one solvent, sulphurous acid. In U. S. Bureau of Mines Report of Investigations 3024 C. W. Davis gives the following experimental data on sulphurous acid dissolution of manganese minerals:

> The samples were crushed in an agate mortar and screened to the desired particle size; 5-gram mineral samples and 1-liter portions of a 3-percent (by weight) SO_2 solution were added to 5-pint bottles which were stoppered and agitated on rolls. Fifty-ml samples of solution were removed from time to time and analyzed to determine the progress of the dissolution. Whenever a sample was taken, 50 ml of a fresh 3 percent SO_2 solution was added to retard the depletion of SO_2. The ratio of solution to sample was such as to make the quantity of SO_2 equivalent to at least five times the manganese present, so that the change of concentration of SO_2 during the test was not great.* * *

The results of tests to show the effect of particle size on the rate of dissolution of manganese minerals and products in sulphurous acid solutions are given in table 66. Preliminary tests indicated that the rapid dissolution of pyrolusite, psilomelane, braunite, roasted rhodochrosite, and roasted manganite would make it difficult to follow the course of the action of finely crushed samples. The tests for these minerals and roasted products are therefore confined to -6 +10 mesh samples. For other minerals -28 +100 mesh samples were found more satisfactory.

The rate of the dissolution may be seen from table 66 and from the curves of figure 18. It is interesting to note that the rate is similar for -6 +10 mesh pyrolusite, psilomelane, braunite, roasted manganite, and roasted rhodochrosite, over 90 percent of their manganese being dissolved in 3 hours. These products apparently could be leached without fine grinding.

The rate of dissolution of hausmannite (-6+10 mesh) during the first 12 days is much slower than that of the products mentioned before and it takes longer to dissolve completely.

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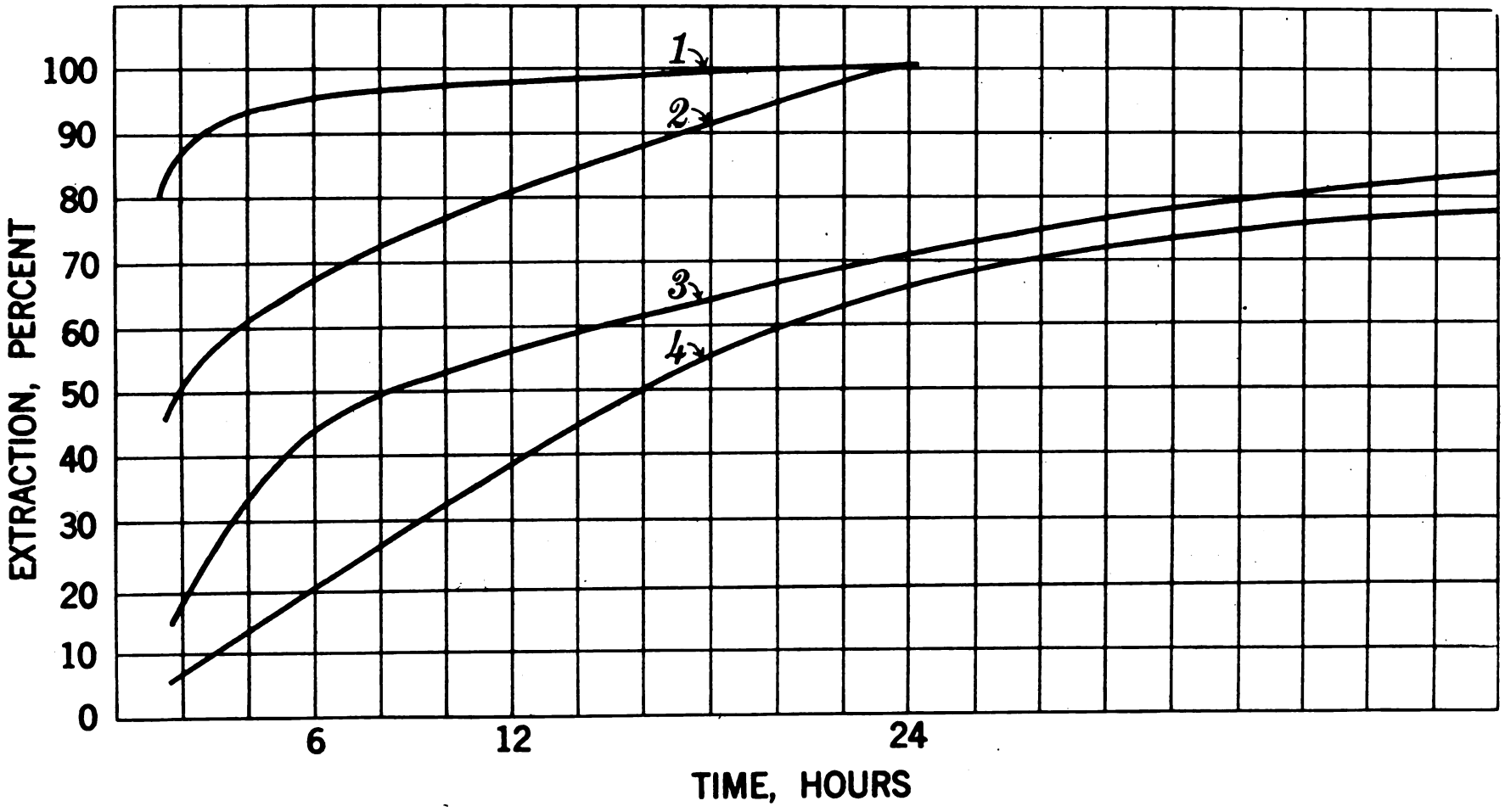

Figure 18.- Rate of dissolution of manganese minerals in 2 percent SO_2 solution: 1, Pyrolusite (-6+10 mesh), psilomelane and others are similar so are not included; 2, hausmannite (-6+10 mesh); 3, manganite (-28+100 mesh); 4, rhodochrosite (-28+100 mesh).

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TABLE 66. - Rate of Dissolution of Manganese Minerals in 3-Percent SO_2 Solutions at Room Temperature (25°C.)

No.	Sample	Mesh		Treatment before leach	Percent extraction of manganese for different time intervals							
		Through	On		30 minutes	3 hours	6 hours	12 hours	24 hours	2 days	4 days	6 days
1	Pyrolusite ..	6	10	None	81.4	92.5	95.0	97.8	100.0	- -	- -	- -
2	Psilomelane .	6	10	do	86.0	95.5	98.1	100.0	- -	- -	- -	- -
3	Hausmannite .	6	10	do	45.8	57.0	67.4	80.4	100.0	- -	- -	- -
4	Braunite	6	10	do	87.8	92.8	96.0	98.2	100.0	- -	- -	- -
5	Manganite 1/.	6	10	do	7.7	12.8	18.9	28.8	42.0	61.2	84.4	92.5
6	do	28	100	do	14.7	24.3	44.5	- -	70.2	85.1	100.0	- -
7	do	6	10	Roasted	75.5	90.4	96.2	100.0	- -	- -	- -	- -
8	Rhodochrosite	28	100	None	6.0	10.5	20.1	38.5	66.0	80.5	90.5	97.3
9	do	6	10	Roasted	84.8	95.2	98.1	99.2	100.0	- -	- -	- -

1/ The manganite broke into elongated pieces such that although they passed a 6-mesh screen their longest dimension was several times as great as their shortest.

Manganite and rhodochrosite are attacked much more slowly, the smaller particles of manganite (-28+100 mesh) requiring 4 days of dissolution and those of rhodochrosite more than 6 days. Roasting such minerals before leaching might be desirable.

Table 67 contains the results of tests to determine the time required to dissolve manganese minerals and roasted products of different sizes at two different temperatures (for the more refractory minerals). In brief, the results show that decrease in particle size and treatment at 40°C. (instead of at 25°C.) increase the rate of dissolution. They also show that fine grinding, in the case of manganite, and fine grinding and heated solutions, in the case of rhodochrosite, reduce the time of complete dissolution of these minerals to such an extent as to be comparable with the time required to dissolve the manganese from -6+10 mesh samples of the other minerals.

Whether it would be better to use a preliminary roast or to depend on fine grinding and hot solutions for treating the more refractory manganese minerals would have to be determined by large-scale tests of the material under investigation.

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TABLE 67. - Effect of Temperature and Size on Rate of Dissolution of Manganese Minerals in 2-Percent SO_2 Solutions

Room Temperature (+25°C.)

No.	Sample	Time for complete extraction					
		-6+10 mesh	-28+100 mesh	-100+200 mesh	-200 mesh	-100+200 mesh	-200 mesh
1	Pyrolusite	16 hours	- -	15 minutes	- -	- -	- -
2	Psilomelane ...	12 hours	- -	do	- -	- -	- -
3	Hausmannite ...	24 hours	- -	2 hours	- -	1 hour	- -
4	do 1/..	- -	- -	30 minutes	- -	15 minutes	- -
5	Braunite	20 hours	- -	15 minutes	- -	- -	- -
6	Manganite	2/6 days	4 days	2 days	16 hours	6 hours	4 hours
7	do 1/ ...	12 hours	- -	15 minutes	- -	- -	- -
8	Rhodochrosite .	- -	3/6 days	4/2 days	2 days	1 day	11 hours
9	do 1/	18 hours	- -	15 minutes	- -	- -	- -
10	Wad	- -	- -	do	- -	- -	- -

1/ The minerals were roasted at 800°C. to give these products.
2/ 92.5 percent of the manganese extracted.
3/ 97.5 percent of the manganese extracted.
4/ 94.0 percent of the manganese extracted.

DISSOLUTION OF MANGANESE IN ORES IN SULPHUROUS ACID

Tests were made to determine whether dissolution of the manganese minerals of various ores could be effected by sulphurous acid solutions. A partial analysis of the ores, with a statement of their source and the results of treatment with SO_2 solution, is given in table 68.

Samples 1 and 2 were commercial metallurgical ores; samples 3, 4, and 5 were concentrating ores from which chemical grade concentrates were used in the manufacture of batteries; samples 6 and 7 usually are classified as manganiferous iron ores and represent material of which large tonnages have been developed; and samples 8, 9, and 10 are from prospects.

The ores were prepared by grinding to -100-mesh. The conditions of testing were as follows: 25-gram samples, 1 liter of 4 percent (by weight) SO_2 solution, and agitation in stoppered bottles on rolls for 16 hours at 25°C.

The results in table 68 show that a satisfactory amount of manganese was dissolved from nearly all of the ores tested and that in only one instance was the extraction notably poor.

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TABLE 68. - Dissolution of Manganese from Ores by Sulphurous Acid

Sample	Source	Percent			
		Mn	Fe	SiO_2	Mn dissolved
1	Crescent mine, Olympia Peninsula, Wash.	49.6	0.87	13.5	100
2	Livermore district, Calif.	45.3	1.4	20.1	100
3	Trout mine, Philipsburg, Mont.	19.4	1.9	18.3	96.3
4	Climax mine, Philipsburg, Mont.	35.4	1.7	26.2	99.3
5	Moorlight mine, Philipsburg, Mont.	25.4	1.2	35.2	94.7
6	Cuyuna district, Minn.	22.4	33.3	25.2	98.2
7	do	4.1	32.4	37.9	98.1
8	Near Silver City, N. Mex.	16.0	35.6	10.5	97.3
9	Near Midas, Nev.	21.2	2.7	68.1	59.8
10	Near Hopeland, Calif.	19.8	2.5	63.9	98.8
11[1]	Kingman district, Ariz.	6.4	2.3	68.5	100
12[1]	Las Vegas, Nev.	21.6	2.0	35.0	100

1/ Added by author.

It would seem that manganese ores containing the common manganese minerals, except rhodonite, can be successfully treated so that a large part of their manganese content is dissolved in SO_2 solution. The results do not warrant a definite statement as to their rates of dissolution, which, even for the same minerals from different sources, might vary greatly owing to differences in physical or chemical composition or to the presence of impurities that might exert electrolytic effects. This uncertainty is illustrated by the results given previously for different specimens of braunite.

BRADLEY PROCESS (40Z)

Under the firm name of Bradley-Fitch Syndicate, Ltd., Wilson Bradley and his associates developed in the Lake Superior mining region an adaptation of ammonia leaching that has received much attention. Their results warrant detailed description. The process was intended primarily for leaching siliceous manganese iron ores of the Cuyuna range, Minnesota, but can be adapted for the treatment of the higher oxides of manganese.

An important feature for the recovery of the manganese is a low-temperature (400°C.) roasting of the ore at 65-mesh in a reducing atmosphere formed by the introduction of hydrogen-carbon monoxide gas and water vapor (35, 36). By close regulation of the roast MnO_2 is reduced to MnO and Fe_2O_3 to the magnetic Fe_3O_4. The calcine must be cooled out of the presence of air to prevent reoxidation. It is then agitated with ammonium sulphate liquor at about 88°C. for 30 minutes. The reduced manganese oxide readily dissolves as manganous sulphate, with generation of ammonia gas. The gas passes to a series of scrubbing towers. The pulp is filtered; and the filtrate containing the manganous sulphate also goes to the scrubbing towers, passing countercurrent

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with an excess of ammonia. Under this condition the ammonia reacts with manganous sulphate to regenerate ammonium sulphate and precipitate manganous hydroxide. By the introduction of air with the ammonia gas the manganous hydroxide ($Mn(OH)_2$) is changed to the more stable manganic hydroxide ($MnO.OH$). It may then be settled, washed, dried, and sintered. The ammonium sulphate remaining in solution is reused to leach a fresh charge of the prepared manganese calcine (MnO).

A double system of digestion or leaching is employed; the liquor from the first tank goes to precipitation, and clean solution is used to finish the leach in the second tank, then this solution is used on a new charge in the first tank. By this method iron impurities are precipitated in the first tank by the fresh ore containing excess manganese oxides. The final residue from the second treatment is passed to magnetic separator for the recovery of the iron.

Pilot Plant

The pilot plant installed at the Minnesota School of Mines (fig. 19) had a capacity of about 4 tons per day. It operated with ore of about this composition: Manganese, 17 percent; iron 29.93 percent; silica, 24.42 percent; alumina, 4.14 percent; lime, 1.0 percent; and phosphorus, 0.06 percent.

The ore was crushed with jaw crushers to 4 inches, screened, then crushed with Symons cone to 1/4 inch and finished with Hardinge ball mill with Dorr classifier in water circuit to pass 65-mesh. The pulp was thickened in a Dorr thickener and dewatered on Dorr filters to about 10 percent moisture. The filter cake was dried in a rotary-type kiln drier using the waste-gas heat from the reducing furnace. A Herreshoff-type furnace was used to reduce MnO_2 to MnO and Fe_2O_3 to Fe_3O_4, the objective being that the calcine contains the minimum amount of MnO_2 because manganese in this form is not soluble in ammonium sulphate; and the minimum amount of FeO because iron in this form is soluble in ammonium sulphate. The best results were obtained with low-temperature (400°C.) roast. The city gas was used as the reducing agent, and it analyzed:

	Percent		Percent
Illuminants	8.4	H	40.1
CO_2	3.2	CH_4	13.8
O	0.3	N	5.3
CO	28.9		

The selective roasting whereby the reduction of MnO_2 to MnO is nearly complete before the iron reduces to FeO is claimed as a Bradley discovery, and the good control of the roasting operation to prepare the calcine is a necessary condition for good leaching results. The hot calcine is cooled out of the presence of air before going to the leaching system.

Flow Sheet

By following the accompanying flow sheet (fig. 19) details of the process may be better understood. Two iron digesters of a tray type 6 to 18 inches

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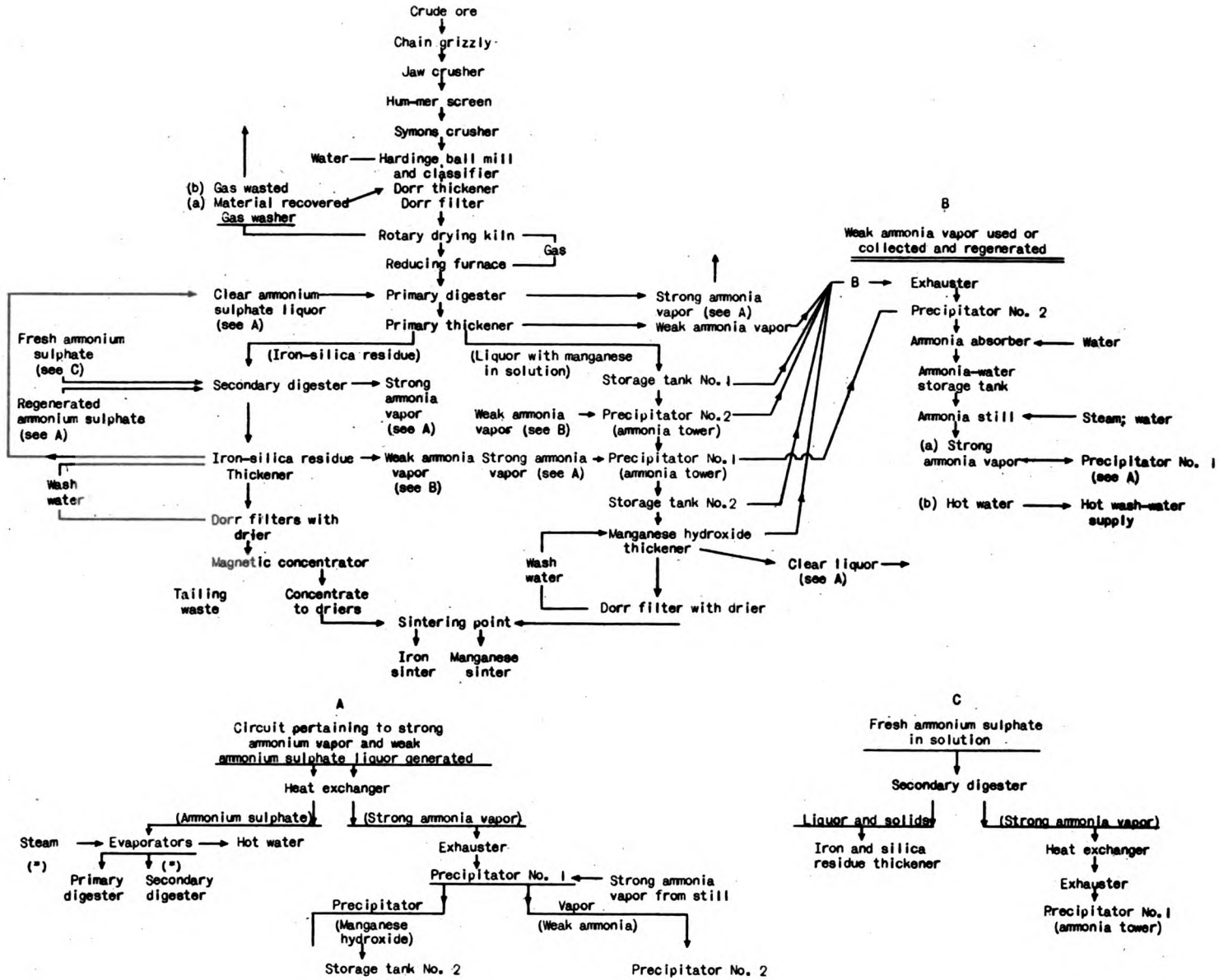

Figure 19.- Bradley process for leaching manganese ores.

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in depth, so made that they can be heated on the bottom, are used in the treatment of the ore for dissolution of the manganese. The plan is to allow maximum surface to permit easy expulsion of ammonia vapor.

The prepared calcine goes to the primary digester, where it is agitated with 5 to 15 parts of liquor containing about 10 percent ammonium sulphate, and as this liquor is a wash advanced from the secondary digester it also contains about 4 percent manganese sulphate in solution and small amounts of iron as impurities.

The amount of liquor used in digestion of the ore will vary with the percentage of manganese to be dissolved. For this reason the percentage of ammonium sulphate and manganous sulphate carried in solution is a better guide to the quantity of solution needed for the best results. The pregnant solutions are held near 6 percent manganous sulphate and 7 percent ammonium sulphate. Only 50 percent of the manganese is precipitated in each cycle.

The time of treatment in the primary digester is about 30 minutes at 88°C. to obtain about 60-percent extraction of the manganese. The ammonia vapor expelled during treatment in the digesters is drawn into the ammonia tower to be used for precipitating manganese from the sulphate solution and for regenerating ammonium sulphate. Most of the iron entering as impurities in the liquor advanced from the secondary digester is precipitated by the excess manganese that remains in the pulp during the treatment in the first digester.

The partly treated pulp from the primary digester, containing in solution about 6 percent manganous sulphate and about 7 percent ammonium sulphate, flows to a separator or filter; the clean solution goes to the ammonia tower and there passes countercurrent with ammonia vapor for the precipitation of about half of its manganese as manganous hydroxide; oxygen (in the air) is admitted with the ammonia vapor, or the precipitate is agitated in contact with air to produce the stable manganic hydroxide (MnO.OH), which is removed by filter and sintered to obtain a product as high as 70 percent manganese. The residue from the filtration of the pulp from the primary digester goes to the secondary digester for continued treatment.

In the secondary digester the partly leached ore is further treated, as in the primary digester, except that liquor from the tower after precipitation plus about 1.5 percent fresh ammonium sulphate is used to insure maximum removal of the manganese. This solution contains about 11.5 percent ammonium sulphate plus 3 percent manganese sulphate. After treatment and filtration the solution is advanced for use in the first digester. The leached tails go to magnetic concentrators for recovery of magnetic iron (Fe_3O_4).

During the leaching periods the solutions at 88°C. dissolve manganese and correspondingly lose free ammonia, and both of the reactions are reversed in the precipitator; that is, a large volume of 10 percent ammonium sulphate solution takes up about 2 percent manganese sulphate in addition to the 4 percent it then held, making a 6-percent pregnant solution, and during this additional dissolution correspondingly loses ammonia, reducing the ammonium sulphate

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content to about 7 percent. Both go to the cooler towers, where passing countercurrent the ammonia precipitates manganese and reenters the solution as ammonium sulphate. The exit solution from the towers containing about 10 percent ammonium sulphate and 3 percent manganese sulphate is built up by the addition of 1.5 percent fresh ammonium sulphate and then used in the second digester to take up virtually all of the soluble manganese remaining in the ore, and in doing so the solution is built up by an additional 1 percent of manganese sulphate.

Washing

Both the residue from the secondary digester and the precipitates from the towers require washing to recover leach solution containing ammonium sulphate and manganese sulphate. The excess water thus added to the system is an important consideration, as it requires expensive evaporation to maintain solution concentration at the economical point. In washing this residue the best results were obtained by the use of vacuum filters; centrifuges are proposed as likely of development.

Magnetic Concentration

The residues from the treatment of Cuyuna manganese ores were treated over a magnetic log washer with indicated recovery of 70 percent total iron in a product containing 3-1/2 percent manganese.

Sintering

It is proposed to sinter both the manganese and the iron byproducts if they are to be used for metallurgical purposes.

Evaporation

Multiple effect evaporators were favored, but on account of cost the simple type of direct evaporation was adopted.

Impurities

In this method of leaching manganese ores the solvent shows a preference for manganese over iron, therefore little or no iron should be dissolved in the primary digester. The iron dissolved during treatment of the low-grade manganese pulp in the secondary digester should, after the solution advances to the primary digester, be mostly precipitated by the excess manganese as ferrous hydroxide and eliminated from solution. If important enough the small amount of soluble iron remaining in the solution may be precipitated with a little ammonia before the solution is advanced to the towers for precipitation of the manganese. Manganese precedes iron in leaching, wherefore iron precipitates more rapidly than manganese from the leach solution.

During the leaching a chemical reaction changes the oxide to a sulphate of manganese with the evolution of ammonia gas.

$MnO + (NH_4)_2 SO_4 = MnSO_4 + 2 NH_3 + H_2O$.

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The manganese in solution as manganous sulphate is separated from the residual ore and pumped to a standard ammonia tower, where it passes countercurrent with ammonia gas released in the reaction. Under the conditions in the tower manganous hydroxide is precipitated.
$MnSO_4 + 2\ NH_3 + H_2O = (NH_4)_2\ SO_4 + Mn(OH)_2$.

The manganous hydroxide reacts with oxygen from the air and readily changes to the partly dehydrated manganic hydroxide
$2Mn(OH)_2 + O = 2\ MnO\ .\ OH + H_2O$.
This stable product is washed, dried, and sintered.

A flow sheet (fig. 20) indicating the principal reactions is given as an aid in following the procedure of the process.

SWEET PROCESSES

Prof. A. T. Sweet and his associates at the Michigan School of Mines, Houghton, Mich., developed two methods for sulphatizing manganese and extracting it from ores. In one method carbonate or lime ores are roasted with ammonium sulphate, and in the other low-lime and relatively high-iron manganese ores are roasted with sulphuric acid to produce soluble manganese sulphates. Both processes depend upon the reaction obtained by roasting the sulphate at a temperature higher than the decomposition point of iron sulphate.

Sweet Ammonia Process

The ammoniacal leach method was developed for beneficiation of the complex carbonate ores that occur along the Missouri river near Chamberlain, S. Dak. The manganese occurs as nodules in shale in the ratio of 1 ton of ore to 10 tons of waste. The nodules or ore show by analysis: Manganese, 16 percent; iron, 11 percent; phosphorus, 0.429 percent; silica, 13 percent; magnesium, 1.87 percent; lime, 15 percent; aluminum, 2.75 percent; loss on ignition, 26 percent. Most of the elements in the ore are intermixed as complex carbonates.

An experimental plant with capacity of 1 ton per day was operated as indicated under the following flow sheet (fig. 21).

A description of the process by Professor Sweet states:

1. The ore was crushed dry. According to the results of a series of tests, crushing to minus 65 mesh gives satisfactory results.

2. The finely crushed material is mixed with the ammonium sulphate, and a little moisture is desirable. The moisture seems to aid in intimately mixing the ore and the sulphate.

3. The mixed pulp is run to the roaster, where the CO_2 is driven off, the sulphate broken up, and the ammonia (NH_3) is liberated. The ammonia and CO_2 are discharged to a tower, collected in the water, and used later on in the process as a precipitant. The sulphate pulp is sent to a countercurrent leaching system.

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4. The leach solution from the first thickener of the countercurrent decantation system is clarified and sent to the precipitation tank. The ammonium carbonate solution from the tower is admitted, and the manganese is precipitated as the carbonate, the ammonium sulphate being thereby regenerated.

5. The precipitated manganese carbonate is sent to filtration and sintered.

6. The washed pulp from the final thickener of the countercurrent decantation system is also washed in carbonate solution, steamed, and washed, with the recovery of the ammonium sulphate for the next leach.

The quantity of reagent used in this process is a function of the manganese content and the amount of CO_2 present in the ore. The time of roast may vary from 30 minutes to 45 minutes, depending on the temperature.

This method is particularly suited for the treatment of manganese carbonate ores because the ammonia, on delivering the sulphate ion to the manganese, joins with the liberated CO_2 to form a desirable precipitant for the manganese which was taken in solution. The temperature of the roast should be kept at about 430°C., as higher temperatures will break up and lose part of the ammonia.

Sweet Acid Process

The second Sweet process is more suitable for ores in which lime and its associated minerals are very low and may contain relatively high iron. The procedure in the operation is easily followed by referring to figure 22.

The steps given by Professor Sweet follow:

(1) The ore was crushed and ball-milled through 65-mesh. The crushing was done dry, though 10 percent moisture in some of the samples did not interfere with the reactions nor with the subsequent roasting operation.

(2) The ground pulp was mixed with sufficient sulphuric acid to take care of the lime and magnesite, together with the small amount of other carbonates which were present. This operation was facilitated by the use of a small concrete mixer. The pulp when properly mixed with the acid was very dry.

(3) The acidified pulp, which was composed of the sulphates of lime, magnesia, manganese, and iron, was introduced into the Herreshoff roasting furnace. This furnace was fired with an oil burner in one of the bottom holes. The temperature at the point of maximum heat was about 790°C.

(4) The roasted product of the furnace, a bright Indian red in color, was cooled and dropped into an agitator, and water sufficient to take

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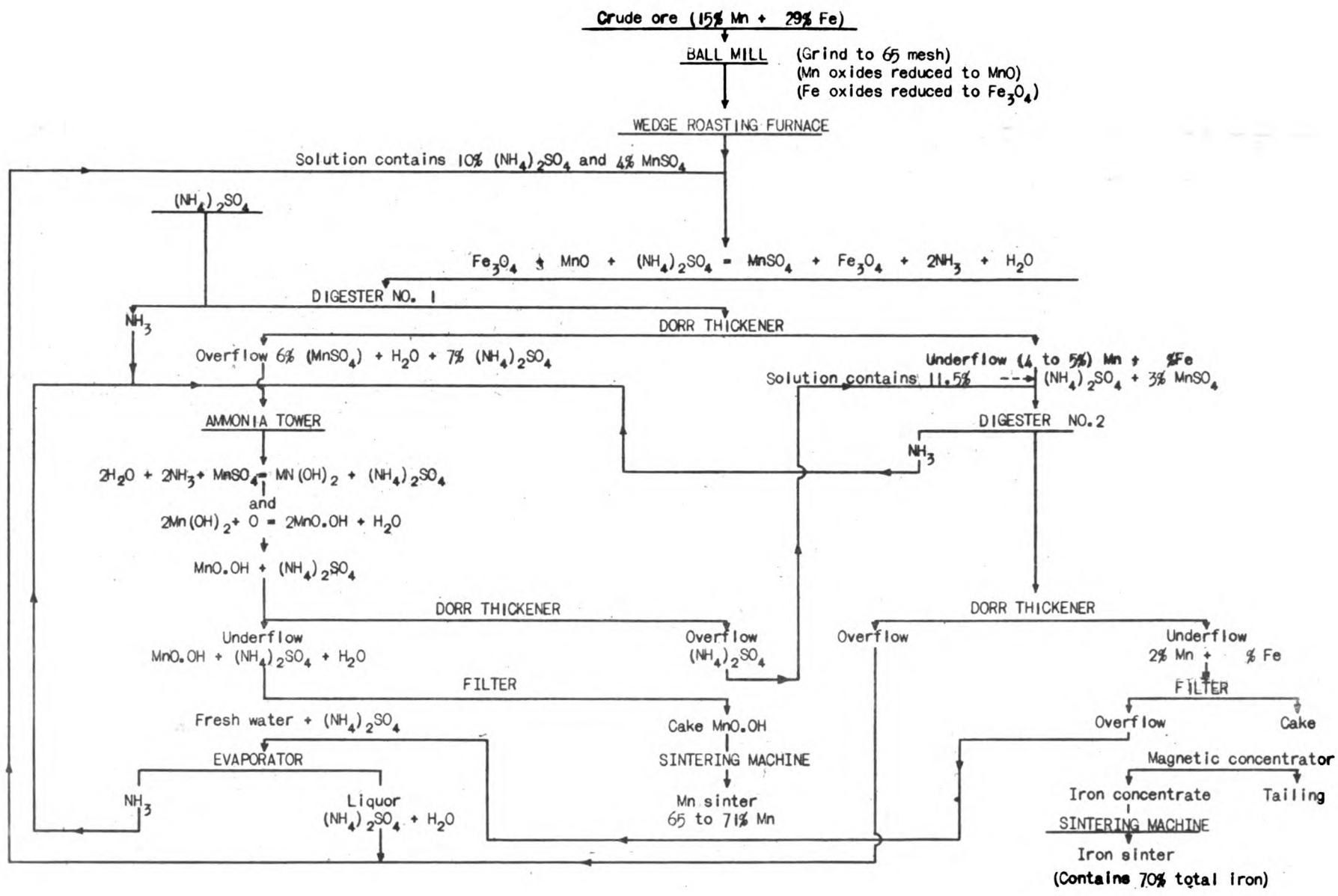

Figure 20.- Bradley leaching process for manganese ores showing principal reactions.

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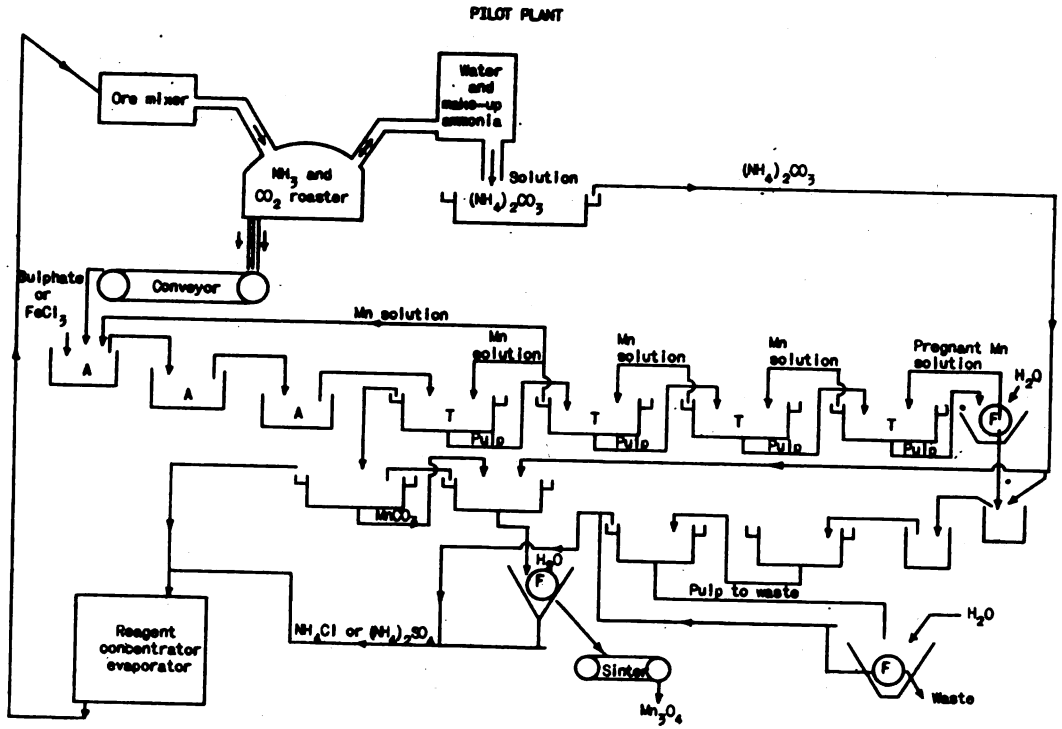

Figure 21.- Sweet ammonia process No. 1 using NH_4Cl or $(NH_4)_2SO_4$.

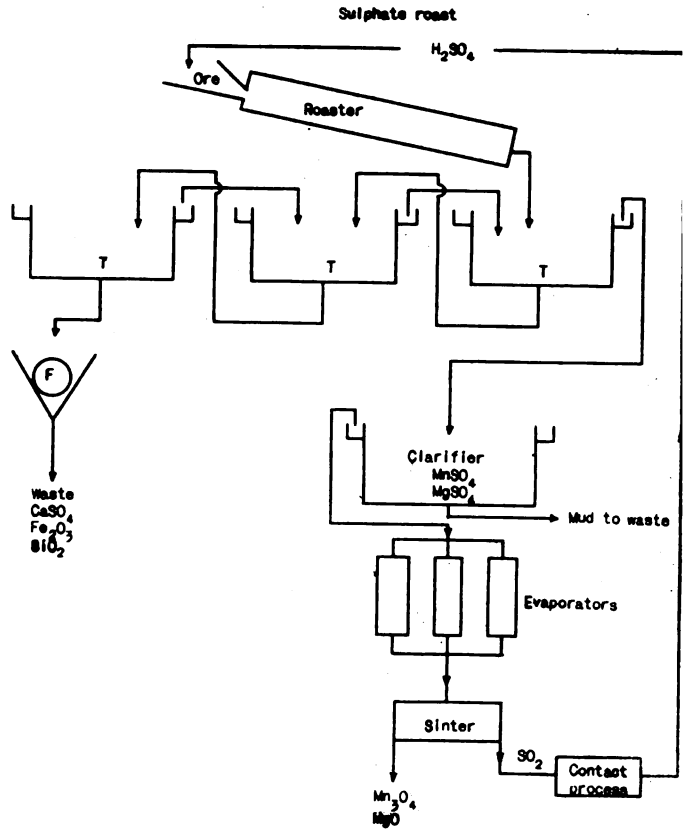

Figure 22.- Sweet acid process No. 2.

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the soluble salts into solution was admitted. The ore was agitated for about an hour and then decanted to the thickeners, where it was washed by countercurrent decantation. The pregnant solution from the first thickener was discharged to precipitation tanks.

(5) A steam coil was arranged in the precipitation tanks, and the solution was evaporated to precipitate the manganese sulphate. The crystals first forming on the precipitation tank were skimmed off by hand and were found very high in magnesium sulphate. Skimming proved to be one method of removing some of the magnesia.

(6) The manganese sulphate from the precipitation tanks, or more properly from the evaporation tanks, was sent to a Dwight-Lloyd sintering machine, which produced a hard, porous sinter assaying on the average about 60 percent manganese, which was present in Mn_3O_4. The sinter contained magnesia and some silica. Very little iron was present in the finished product, and the phosphorus was very low. It was impossible to save the SO_3 in the sintering operation in the laboratory, but its reclamation offers only a mechanical difficulty which should be overcome.

The special feature in the process is the roasting with sulphuric acid above the temperature needed to break up any iron sulphate that may be formed. The disadvantages are the cost of acid and the cost of evaporating the sulphate solution.

Typical Examples of Sulphatizing Process

(1) South Dakota Manganosiderites

Sample	Percent				
	Mn	Iron	Silica	Lime	Phosphorus
Head assay	26.0	13.3	10.5	20.0	0.40
Residue	.4	24.0	13.1	50.0	.58

NOTE.- The "residue" in the above and following tables refers to the pulp remaining after the leaching of the manganese sulphate.

This table shows an extraction of well above 90 percent, but because of the high lime content the acid loss is excessive.

(2) Lake Superior Iron Ore

Sample	Percent				
	Mn	Iron	Silica	Lime	Phosphorus
Head assay	17.5	35.2	12.3	.45	0.05
Residue	.3	51.0	15.8	.72	.06

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This, of course, is a good extraction, and the low loss of acid due to lime and magnesia is a desirable feature of the ore. The iron contained some sulphur because of the incomplete extraction of the manganese sulphate. Sintering of the finely divided iron, however, is possible and results in the removal of the sulphur.

Sweet Chloride-Leach Process

Professor Sweet also experimented with a third process, which he calls "chloride leach." It is not thought to have any particular advantages over his sulphuric acid process and he does not indicate its importance. The method, with flow sheet (fig. 23), is given because it examplifies the large amount of thought that has been given to chloride leaching.

The process is best explained in Professor Sweet's words as follows:

Hydrochloric Acid and Soluble Chloride Processes

Numerous attempts have been made to use hydrochloric acid as a solvent for manganese, the chief obstacle in the way being the presence of the calcium compounds in the ore. As in the case of sulphuric acid, the calcium forms a very stable compound with the acid and consumes so much of the reagent that it makes its use prohibitive. With the ore low in lime and allied elements the process has the advantage of being able to extract the manganese without the iron in a very easily controlled operation. As is true when sulphuric acid is used, the addition of raw ore to the pregnant solution from the final thickener reduces the iron content of the solution to practically nothing.

The ore need not be crushed to as fine a mesh as is necessary in the use of sulphuric, for the chloride of lime is very soluble and thus forms no protective coating which delays solution.

Crushing to 10-mesh and subjecting the ore to the leach solution, agitating, thickening, and washing are the steps in the process of removal. Ore is added to the circuit at the point where the pregnant solution leaves for precipitation. The waste which is taken out of the final washing tank may contain enough iron to be a valuable byproduct. Ferric chloride may be substituted for hydrochloric acid with very satisfactory results. Ammonium chloride under special conditions also takes the manganese into solution.

LEAVER DRUM-LEACHING PROCESS

This process is described in Bureau of Mines Bulletin 173. A patent (U. S. Patent 243015) was granted to E. S. Leaver November 18, 1918. It is based on the rapid dissolution of the various higher manganese oxides, especially pyrolusite, psilomelane, and wad, in hot sulphurous acid formed by introducing hot furnace gas containing 2 to 6 percent SO_2 (by volume) countercurrent to a pulp flow having a consistency of 2 of water to 1 of ore crushed to about 20-mesh. The carbonate of manganese is made soluble in sulphurous acid by roasting; the silicate is insoluble.

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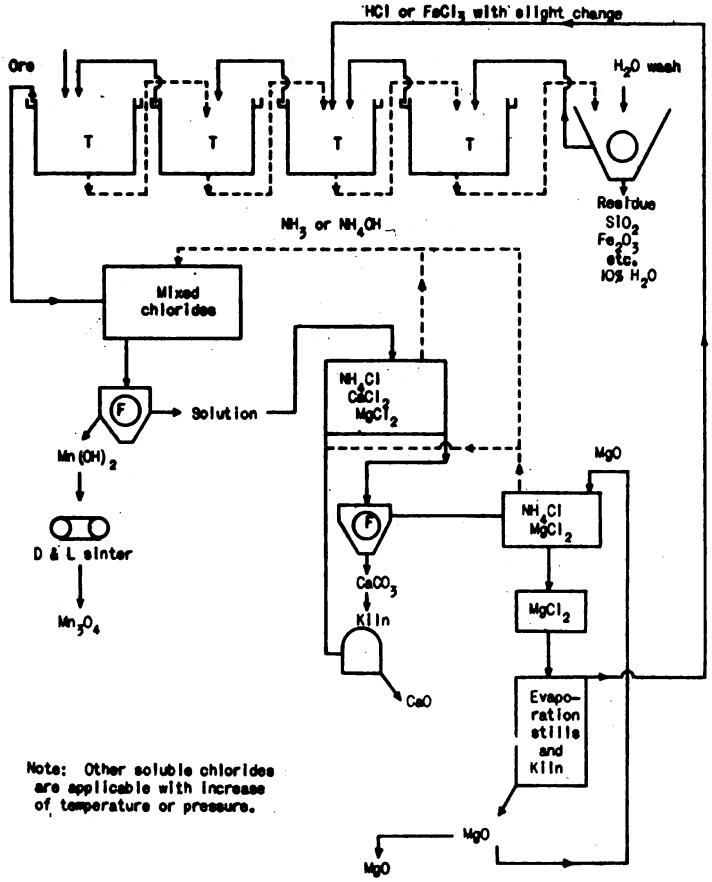

Figure 23.- Sweet chloride process No. 3; chloride leach.

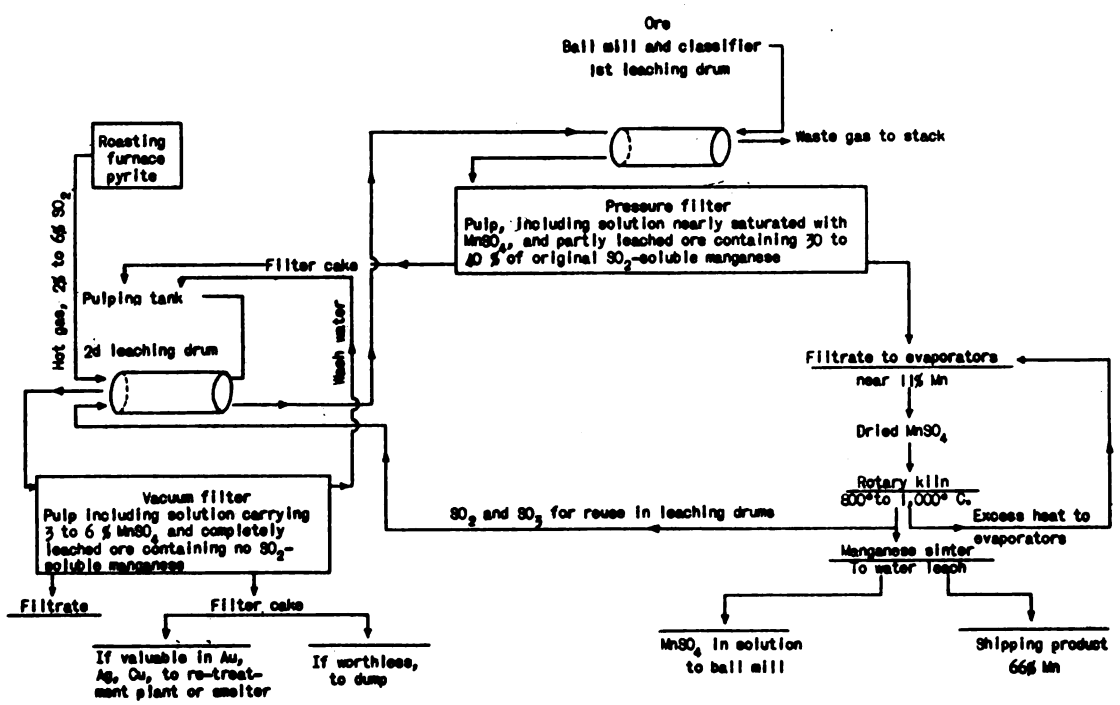
Ore
Ball mill and classifier
1st leaching drum
Waste gas to stack
Roasting furnace pyrite
Hot gas, 2% to 6% SO2
Pressure filter
Pulp, including solution nearly saturated with MnSO4, and partly leached ore containing 30 to 40 % of original SO2-soluble manganese
Filter cake
Pulping tank
2d leaching drum
Wash water
Filtrate to evaporators
near 1% Mn
Dried MnSO4
Rotary kiln
800° to 1,000° C.
Vacuum filter
Pulp including solution carrying 3 to 6 % MnSO4 and completely leached ore containing no SO2-soluble manganese
SO2 and SO3 for reuse in leaching drums
Excess heat to evaporators
Manganese sinter to water leach
Filtrate
Filter cake
If valuable in Au, Ag, Cu, to re-treatment plant or smelter
If worthless, to dump
MnSO4 in solution to ball mill
Shipping product 66% Mn

Figure 24.- Leaver drum-leaching process.

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The dissolution of the manganese minerals is effected in the Leaver drum (fig. 24). A double-drum system is recommended. The pulp enters one end of the drum, and the hot waste furnace gas containing SO_2 enters the opposite end of the drum. Intimate mixing during the countercurrent flow results in the pulp becoming progressively warmer until it exits at about 45° C., at which temperature it retains practically no free SO_2 gas. All the dissolved manganese is in the form of the sulphate when the pulp flows from the drum.

By the use of tandem drums the iron and phosphorus that dissolved in removing virtually all the manganese during treatment in the second drum will be precipitated on returning this solution to the new charge in the ball mill or the first drum. This is explained by the changed condition in the operation. The advance solution is used to pulp fresh manganese ore and immediately loses its slight acidity in dissolving manganese. In this neutral solution, the remaining large excess of undissolved manganese, having a greater affinity for the sulphate iron, readily replaces the iron and phosphorus. The precipitated iron and phosphorus become part of the residual ore flowing through the circuit.

The pulp discharge from the first drum should pass to a pressure-type filter for separation of the almost saturated solution (manganese sulphate) and the partly leached ore to be repulped for continued treatment in the second drum. The filtrate is crystallized or evaporated by using waste heat from the furnace. The resultant sulphate is roasted by a direct flame in a rotary-type clinker furnace at a temperature of 825° to 1,000° C. The calcined product should run from 60 to 64 percent manganese. The SO_2 and the SO_3 existing with the furnace gas may be reused in the leaching drum. This process, the essential features of which were worked out for the Phelps Dodge Corporation by G. D. van Arsdale and C. G. Maier (U. S. Patent 1348068) was used at the Copper Queen Smelter at Douglas, Ariz., in 1918 on a 10-ton experiment plant for leaching an oxidized manganese-silver ore.

Better understanding of the details in the operation of the proposed double-drum system can be obtained from the flow sheet (fig. 25).

Ball Mill

The oxidized manganese ores or the calcine from the roasted carbonates after primary crushing are fed to a ball mill for wet crushing to 20 mesh in circuit with a classifier. The leach filtrate from the second drum in the circuit is the solution used in the ball mill. It carries 3 to 6 percent of manganese as manganous sulphate and the impurities that are dissolved in completing the leaching of the manganese ore, and it is practically neutral. On contact with a large excess of fresh manganese dioxide ore most of the impurities, including the dissolved iron and phosphorus, are precipitated in the pulp within the ball mill.

Leaching Drum No. 1

The overflow pulp from the ball-mill classifier goes to the first leaching drum for the preparation of an almost saturated solution of manganous sulphate (nearly 11 percent). This is accomplished by intimate contact between the mineral particles and the SO_2 of the furnace gas by breaking the pulp into a fine spray throughout the length of the drum and passing the gas countercurrent with the flow. For better understanding of the operation a description of the drum erected by the Miami Copper Co. is given (fig. 24).

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This drum was 7'4" inside diameter by 40'0" inside length and had a rated capacity of 100 tons per day for leaching oxidized copper ores. It was built of fifty-four 3-by 6-inch redwood staves bound with iron hoops and set horizontally, revolving at 14 r.p.m. On the inside center of each stave a groove was cut at an angle of 30° to hold the lifters, which were made of 1½- by 4¾-inch lumber and fastened to the stave with wooden dowel pins. On the inside length of the drum thirty-eight 2-inch circular vertical baffles were set 1 foot apart and extended to the inside circumference. Each of these baffles contained ninety-nine 4-inch holes set staggered in four circles, each hole in the outer circle set directly under one of the 54 lifters.

The half of each 4-inch hole toward the center was cut square, and through each of the 99 holes in the vertical baffles extended a longitudinal baffle of 2- by 4- by 38-inch lumber, held ridigly in place by wooden pins.

In the center of each vertical disk or baffle a circular hole 24 inches in diameter was provided as a manway for inspection or repair. On the circumference of this 24-inch circle were equally spaced 14 pieces of 2- by 4- by 38-inch lumber, fastened by wooden pins to each vertical baffle. This passageway along the center of the drum was closed at regular intervals by solid 20-inch wooden disks to divert the gas flow and cause part of the gas to flow alternately from the center toward the circumference and back through the next section. The 20-inch disks were easily removed for inspection, although there was little need for entering the drum. The pulp enters the drum through a gas stack provided to exit the waste gas. The movable joint connecting the stack and drum was sealed quite satisfactorily by the use of two 36-inch by 4½-inch auto tires on which were bolted two machined plates. These plates formed the seal, and the tires allowed for both horizontal and vertical movement. On the pulp exit end, which is also the hot-gas intake, a trap is provided to seal the pulp discharge, and a special design cast-iron seal with asbestos packing joints, allowing for both vertical and horizontal movement was provided by Allis Chalmers Co. The drum was supported by two 18-inch by 8-foot inside-diameter iron castings and held in place by double tapering wedges driven between the outside of the drum and the inside of the casting. The 2-inch vertical disks within the drum were doubled at the point of the carrying castings. On the circumference of each casting 90-pound iron rails were trued to the circle and fastened by set-screws; the circular rails revolved on 30-inch car wheels, two sets on each side in trunnion form.

The drive shaft extended through both sets of car wheels on one side of the drum and by friction between the revolving car wheels and the circular rail satisfactorily turned the drum. The accompanying diagram (fig. 24) shows construction details.

The pulp is lifted by inside buckets similar to a tailings wheel; as the buckets empty and the pulp splashes over each of the longitudinal baffles the SO_2 gas passes directly into the spray through the half-circle opening in the vertical baffles. Under this condition highest absorption of the gas is obtained as the pulp enters one end of the drum cold, this permitting almost complete utilization of the SO_2 before the furnace gas exits at pulp intake of no. 1 drum.

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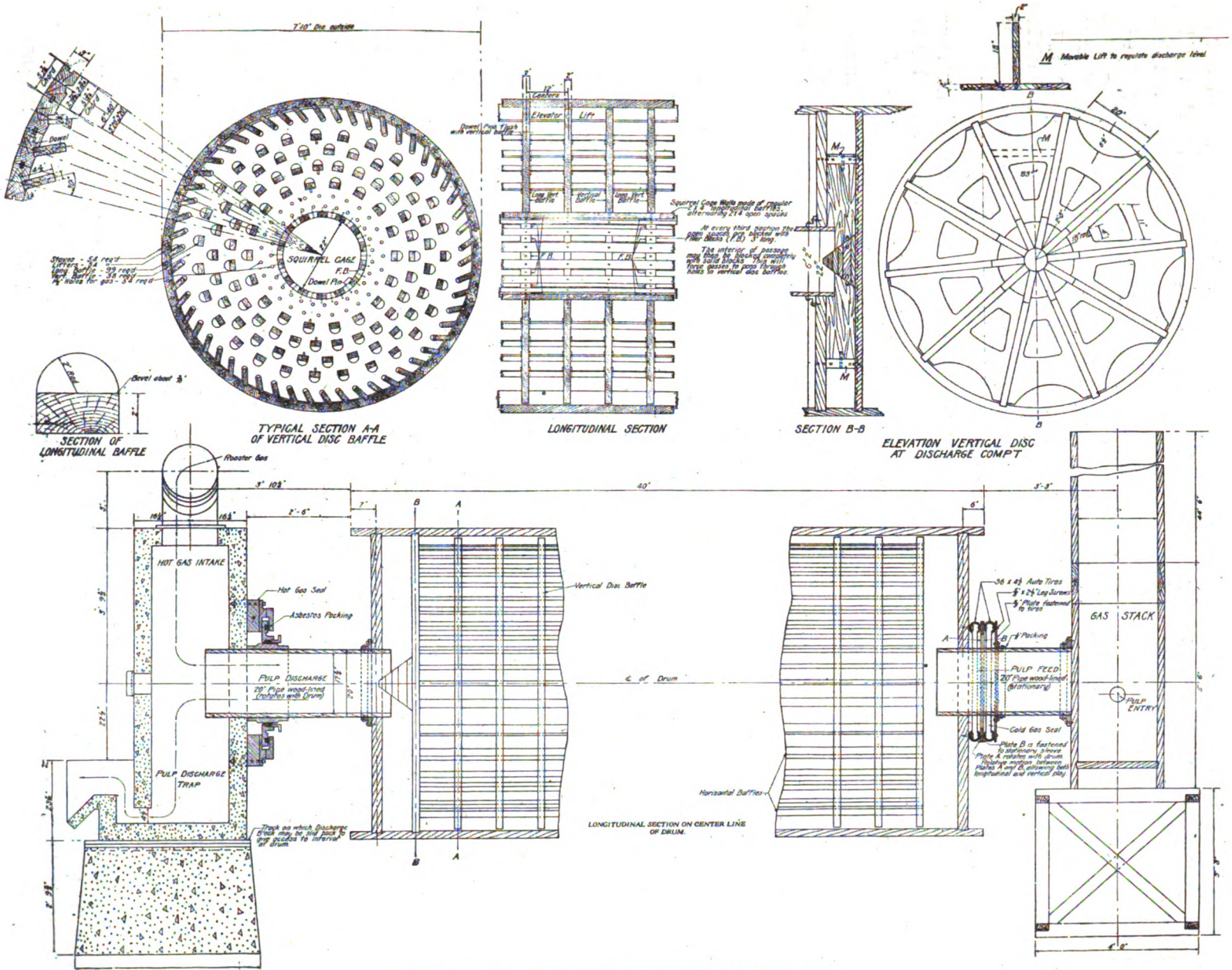
7'10" Dia. outside
SQUIRREL CAGE
Dowel Pin
Sleeves - 54 req'd
Liner Baffle - 27 req'd
Vane Baffle - 54 req'd
Bevel about ¾"
SECTION OF LONGITUDINAL BAFFLE
TYPICAL SECTION A-A OF VERTICAL DISC BAFFLE
Casters
Elevator Lift
Dowel Pins Track with vertical Lifts
Squirrel Cage Plate made of Circular & Longitudinal Baffles, alternating 2"x4" open spaces
At every third section the open spaces (F.B.) 3" long.
The interior of passage may also be blocked completely with solid blocks thru which force passes to pass through holes in vertical disc baffles.
LONGITUDINAL SECTION
SECTION B-B
M Movable Lift to regulate discharge level
ELEVATION VERTICAL DISC AT DISCHARGE COMPT
Rooster Gas
HOT GAS INTAKE
Hot Gas Seal
Asbestos Packing
PULP DISCHARGE 20" Pipe wood-lined (notches with Drum)
PULP DISCHARGE TRAP
Track on which Discharge Grate may be slid back to give access to interior of drum.
Vertical Disc Baffle
℄ of Drum
LONGITUDINAL SECTION ON CENTER LINE OF DRUM.
Horizontal Baffles
36 x 4½ Auto Tires
⅝" x 2½" Lag Screws
¼" Plate fastened to tires
¼" Packing
GAS STACK
PULP FEED 20" Pipe wood-lined (stationary)
PULP ENTRY
Gold Gas Seal
Plate B is fastened to stationary sleeve. Plate A rotates with drum. These are held between plates A and B allowing both longitudinal and vertical play.

Figure 25.- Details of Leaver SO_2 leaching drum.

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During treatment in no. 1 drum it is planned to dissolve only 60 to 70 percent of the soluble manganese. With an excess of readily soluble manganese and SO_2 gas and a limited ratio of solution to ore the pulp exit solution is saturated with manganous sulphate. It is difficult to filter this nearly saturated solution from the pulp; vacuum filters are not satisfactory, and pressure-type filters should be used.

The filter cake from no. 1 drum is repulped with fresh or wash water solution and similarly re-treated in no. 2 drum, except that the hot SO_2 gas direct from the furnace first passes through this drum, and the exit cool gas, still containing a large excess of SO_2, is used for dissolution of the new charge in no. 1 drum. The pulp exiting from no. 2 drum is hot, about 45° C., at which temperature the solution contains practically no free SO_2 and is neutral. The solution in this pulp contains only 3 to 6 percent manganese as manganous sulphate and does not present a difficult filtering problem; vacuum filters may be used. The residue is wasted or retained for its gold or silver value. The filtrate goes to the ball mill for reuse on a new charge of ore.

Pregnant Solution

The manganese is recovered from the almost saturated solution of manganous sulphate by crystallization or evaporation. The resulting sulphate is roasted by direct flame in a rotary-type clinker furnace at 825° to 1,000° C. The calcine from the roaster is hard, compact clinker. It may contain a small percentage of manganous sulphate, which can be removed by leaching with water. The product at the Douglas plant ran 60 to 64 percent manganese.

In the evaporation of the pregnant solution a problem in corrosion was found to be due to the action of ferrous sulphate and liberated sulphuric acid; leaching in two stages presents a simple solution of this difficulty. As sulphur dioxide has a marked affinity for manganese over that shown for uniting with iron, and as only 60 percent of the manganese in the ore pulp is dissolved in the first drum treatment the remaining 40 percent of manganese insures the dissolution of no iron, and the resultant pregnant liquor will not corrode the iron evaporation pans.

Sulphur Dioxide

The success of this process depends on cheap sulphur dioxide. It may be obtained as a waste product in various smelting operations, also by the roasting of iron pyrite or other sulphides which contain enough lead, copper, silver, gold, or other metals to give the calcine a market value, and by the reuse of the SO_2 and SO_3 in the waste gas from calcining the manganese sulphate.

Plant Control

Analytical methods for plant control, including the determination of SO_2 in pure SO_2 solution, SO_2 and sulphites in drum solution, sulphuric acid content of drum solution, total acidity, SO_2 in furnace gas and acid requirements of ores, are given on pages 77 to 81 of Bureau of Mines Technical Paper 312.

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Application

It is recognized that evaporation of the manganese sulphate solution is the expensive part of the proposed process, and conditions must be favorable to compete with imports of high-grade ore. The best chance for success appears as an auxiliary process where the residues may contain other valuable minerals, such as copper, silver, lead, or gold. As carried out at Douglas the process was very nearly a technical and commercial success and might be applicable under favorable conditions in normal times.

WESTLING NITRATE PROCESS

The Westling nitrate process, covered by U. S. Patent 1520079 of July 22, 1924, was used by the American Manganese Products Co. at its plant near Redwood City, Calif. After fine grinding oxidized manganese ores were agitated in tanks similar to the Pachuca type, while the pulp was digested with sulphur dioxide and some air to produce sulphates. The charge was transferred to settlement tanks to remove the coarse particles. The solution and suspended material were separated by an Oliver filter. Powdered calcium carbonate was used to precipitate iron and other impurities from the pregnant solution at 50° C. Calcium nitrate was then added and the solution heated in open pans to separate out the calcium sulphate, which was removed by the Oliver filter. The solution containing manganese nitrate was heated under pressure and thus modified into manganese dioxide and nitrous gases. The nitrous gases were reclaimed by means of scrubbing towers. The manganese dioxide product is of chemical grade, but it did not find a ready market and apparently is not suited for the dry-battery industry.

PROPOSED PROCESSES

The Rare and Precious Metals Experiment Station of the Bureau of Mines has recently conducted small laboratory experiments on combinations of various methods that may aid in improving former proposed processes. Four methods were considered as offering the best possibilities.

No. 1. The original Leaver drum process as given in Bureau of Mines Bulletin 173.

No. 2. Dissolve with waste smelter gas (SO_2) to obtain manganese as sulphate. Precipitate with ammonia plus air to obtain $Mn(OH)_3$ and ammonium sulphate, filter out manganese hydroxide, boil the filtrate with lime (CaO) to expel ammonia, which is reclaimed by scrubbing towers for reuse, discard calcium sulphate, and calcine $Mn(OH)_3$ to obtain Mn_xO_y.

No. 3. Dissolve with SO_2 to obtain manganese sulphate. Add calcium chloride while solution is on the ore to make $MnCl_2$ and $CaSO_4$, filter, add $Ca(OH)_2$ to the filtrate, and agitate with air to precipitate oxides of manganese and regenerate calcium chloride for reuse; calcine the manganese precipitate.

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Table 69.- Comparison of four methods suggested for study in improving hydrometallurgy of manganese

Process	(1) Leaver drum SO_2 leaching	(2) Ammonia	(3) Chloride	(4) Sulphite
Reduction	In first three schemes the original ore is treated direct for dissolution of all minerals except rhodochrosite, which must be given a preliminary oxidizing roast. Rhodonite is untreatable by SO_2 methods.			Reduce Mn compounds to MnO by reducing roast.
Dissolving manganese	Dissolving is done by SO_2 plus water in all four schemes. In first three schemes give double leach.		In Rocky Mountain States waste SO_2 is available. Add $CaCl_2$ while in solution on ore to make $MnCl_2$ and $CaSO_4$.	Mn in solution as $MnSO_3$; must exclude air.
Solutions: Purification, Filtration Concentration Transformation	In all cases iron may be precipitated preferentially by ground limestone. $MnSO_4$ soluble up to 420 grams per liter at 49° C. As concentrated solution made as can be separated from ore. Above sp. gr. 1.2 separation difficult; requires pressure filter.	A conveniently strong pregnant solution made that is fairly readily separable from ore.		SO_2 from furnace dissolved in water, then pure SO_2 expelled by steam for dissolution of manganese as sulphite.
Precipitation; regeneration of precipitant	Solution evaporated to dryness (in spray drier). Nearly dry $MnSO_4$ removed.	Add NH_4OH. $Mn(OH)_3$ precipitated on agitating with air as more easily filtered than $Mn(OH)_2$. Boil $(NH_4)_2SO_4$ solution with CaO. Absorb NH_3 in fresh solution. Discard $CaSO_4$.	Add $Ca(OH)_2$ plus a little NaOH to keep OH^- concentration high. Agitate with air. Regenerated $CaCl_2$ returned to fresh batch ore; MnO_2 precipitated.	Heat $MnSO_3$ solution to expel SO_2 and precipitate $Mn(OH)_3$ or $MnSO_3$; reuse SO_2. In experiments some $MnSO_4$ was formed.
Treatment of precipitate	Calcine $MnSO_4$ to Mn_xO_y and SO_2 and SO_3.	Calcine $Mn(OH)_3$ to Mn_xO_y.	MnO_2 carefully - dry.	$Mn(OH)_3$ or $MnSO_3$ calcined to Mn_xO_y.
Regeneration of solvent	Return SO_2 to releach fresh batch. Return SO_3.	No regeneration of solvent. Both the Ca and SO_2 added discarded to waste as $CaSO_4$.		Return SO_2 to leach fresh batch or ore.

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No. 4. Roast with producer gas to reduce manganese minerals to MnO, leach with SO_2 out of the presence of air or oxygen (the SO_2 in furnace gas would need to be absorbed in water and expelled by steam as used) to obtain manganese as sulphite. Heat pregnant solution to expel SO_2 and thus precipitate manganese as sulphite or hydroxide, reuse the SO_2 and calcine the manganese product.

It is not contended that any methods proposed are practical under the present general conditions. Special local conditions that supply the needed chemicals at nominal cost or offer a market for a particular product may present an opening as a profitable operation.

The four methods are compared in table 69.

RECOVERY OF MANGANESE FROM SULPHATE SOLUTION

A cheap method for the recovery of manganese from the sulphate solution would very much aid the hydrometallurgy. This problem has been given much thought with generally negative results.

ELECTROLYSIS OF MANGANESE SULPHATE SOLUTION

The usual electrolysis failed because the manganese that deposited on the cathode readily redissolved in the acid formed. Attempts to protect the manganese by simultaneously depositing iron with the manganese on the cathode did not aid appreciably. Our experiments show that when an electric current is passed through a solution of manganese sulphate metallic manganese tends to deposit on the cathode, and more or less manganese dioxide is formed at the anode. It is, however, exceptionally difficult to obtain a high current efficiency at the cathode and to produce a satisfactory metallic deposit. A high current efficiency of MnO_2 formation at the anode is readily obtained.

A diaphragm seems to be necessary to separate the anode and cathode. The solution surrounding the cathode tends to become alkaline, and unless this solution is slightly acid manganese hydrate is deposited upon the cathode. On the other hand, the metal deposit is readily dissolved by an acid solution unless sufficient potential and current density are maintained at the cathode. For good results the solution must be exceptionally pure, and the concentration of acid and manganese sulphate in the catholyte must be maintained at a definite level. The presence of ammonium sulphate appears to be beneficial.

The best laboratory results were obtained as follows: A rotating nickel anode was enclosed in a cylindrical alundum diaphragm and surrounded by a cylindrical platinum anode. The catholyte contained 5.5 percent manganese as sulphate, 8 percent ammonium sulphate, and 0.04 percent free sulphuric acid. The acidity was maintained by supplying fresh solution containing 0.21 percent free acid at a rate sufficient to compensate for the electrolytic migration of the acid radical. The current density was 100 amperes per square foot of cathode area. A potential of 5 volts was required; the temperature of the electrolyte was 25° C. Under these conditions a good cathode deposit was

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obtained, and the weight of metal formed indicated a current efficiency of 72 percent. If the electrolysis is continued much over an hour, however, some of the metal is apt to scale and drop off the cathode and redissolve in the acid electrolyte. This difficulty was not overcome, partly because of the difficulty in maintaining exactly the proper acidity in the catholyte.

Manganese dioxide is usually formed at the anode. The nature and amount of the dioxide deposit depend primarily on the kind of anode used and secondarily on the current density, temperature, and composition of the anolyte. High current density, high temperature, and high acidity favor the formation of manganese dioxide. On a platinum anode a dense, lustrous crystalline variety of dioxide is deposited. On anodes of other material, including graphite, carbon, lead, and manganese dioxide, the dioxide produced is usually amorphous.

To summarize; under suitable conditions metallic manganese can be electrolytically deposited from manganese sulphate solution, with or without simultaneous production of considerable manganese dioxide at the anode. No procedure was found, however, by which the metal could be retained and preserved on the cathode during an operating period greatly exceeding 1 hour.

PRECIPITATION OF MANGANESE DIOXIDE OZONE

Ozonized air, passed through a solution of manganese sulphate precipitates manganese dioxide according to the reaction

$$MnSO_4 + O_3 + H_2O \longrightarrow MnO_2 + H_2SO_4 + O_2.$$

With adequate dispersion of the ozonized air in the solution, high utilization of the ozone is possible, but the cost of producing ozone was found to be so high that there is little prospect of using the method commercially to produce manganese dioxide.

BYPRODUCT PROCESSES

French Process

A. G. French has taken out United States Patents 1055157-8 under date of March 4, 1913. The outstanding feature in his process is the recovery of manganese dioxide from the sulphate solution by electrolysis. He proposes roasting sulphide ores containing manganese and zinc at 700° C., then mixing the calcine with 5 percent sodium bisulphate, grinding in water, and leaching to obtain the sulphates of manganese and zinc. After some purification this solution is electrolyzed between anodes of lead and cathodes of zinc. As the zinc is deposited on the cathode a corresponding amount of manganese is deposited at the anode as the dioxide. This could be made a source of considerable manganese dioxide, except that the product contains enough lead to prevent its use in the usual dry-cell battery and it has found very little sale in the chemical or paint industry. Our experiments show that part and probably most of the lead that appears as an impurity in this manganese mud was introduced through decomposition of the lead anode.

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The only present use of this manganese dioxide mud is for oxidizing iron, arsenic, and antimony, so they are precipitated by hydrolysis from the leaching solutions in the electrolytic zinc process. Ralston (311) gives an excellent review covering recent litigation for the manufacture of manganese dioxide in electrolytic zinc practice.

Weldon Process

As early as 1866 the utilization of manganese was associated with the chemical industry, when manganese dioxide was employed in the manufacture of chlorine. The recovery of the manganese from the byproduct, the chloride of manganese, is known as the "Weldon process." Like most inventions, it is largely founded on previous experience and has been perfected by successive improvements. The waste still liquors are neutralized with limestone, and the milk of lime is then added in excess to precipitate all the manganese as the hydrate. The mixture is agitated with air, the reaction is rapid and heat-producing, and more manganous chloride is added to reduce the proportion or excess of quicklime; the resultant dark-brown precipitate, known as "Weldon mud," is mostly manganite of calcium (MnO_2CaO). The washed mud is pumped back to the chlorine generator, in which its reuse is similar in action to that of the original manganese dioxide and quicklime. A complete description, with a diagram of the apparatus used, is given in Thorpe's Chemical Dictionary, pages 13-18.

Various flotation experiments made by the author with the thought of removing the impurities from Weldon mud were unsuccessful. The use of barium hydroxide in the place of calcium hydroxide for precipitation of manganese from the sulphate solution gives a product from which the manganite of barium can be largely separated from the barium sulphate by careful hydraulic classification.

Other Methods Recorded by Patents

United States Patent 1415395 was granted to Chas. J. Reed, May 19, 1922, covering a process of making manganese dioxide from the sulphate. He proposes fusing manganese sulphate containing 2 or more molecules of water with just enough sodium nitrate to combine with the sulphate radical of the manganese sulphate. During the fusion the volatile oxides of nitrogen are expelled and recovered by condensation as byproduct or for reuse. The solid products of the reaction comprising manganese dioxide and sodium sulphate are discharged hot. After cooling the mass is broken up and leached with water. The sodium sulphate dissolves, leaving the manganese dioxide as the final residue.

United States Patent 1770791 was granted to Geo. N. Lebby and Geo. D. Knight, July 15, 1930, for a sulphur dioxide method of leaching manganese ores, including a nitrate process for the recovery of manganese dioxide from the manganese sulphate. It appears to be intended as an improvement on the Westling process as used near Redwood City, Calif. They propose digesting the fine manganese ore in a series of three tanks, passing SO_2 gas through each tank in the series. As each tank is successively charged with enough SO_2 to dissolve

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the manganese it is shut out of the circuit. Magnesium carbonate in the form of magnesite is added, and by the aid of air blown through the charge the iron and phosphorus are precipitated. At this stage in the operation, enough magnesium nitrate is added to react with the manganese sulphate; the charge then goes to filtration. If the filtrate contains copper it is precipitated by aluminum dust. The clean solution flows to the first evaporator, where it is concentrated to a specific gravity of 1.6. The concentrated solution is pumped to a retort and there heated from 200° to 500° C. until the manganese sulphate and magnesium nitrate react and form magnesium sulphate and manganese nitrate. The manganese nitrate is in turn converted into manganese dioxide and nitrous gases. The nitrous gases are oxidized by air to nitric oxide before the gas is passed to the condensing towers. The towers are filled with lump magnesite, with which the nitric acid reacts to form magnesium nitrate for reuse. The hot solution charge from the retort is filtered and washed to remove magnesium sulphate, which may be saved as a byproduct (epsom salts), if the market warrants the extra expense. The manganese dioxide residue remaining on the filter is the final product. The well-recognized disadvantage in this process, in addition to the cost of mechanical operation, is the excessive cost of nitrates. In the handling of the relatively large quantity of nitrates needed to react with the manganese extracted from the ore it has not been practical to prevent losses of nitrogen that have precluded the commercial use of nitric acid processes.

United States Patents 1266731-2 were issued to Geo. C. Westby, May 21, 1918. Each patent covers mechanical equipment for a proposed SO_2 leaching process. In the first patent he proposed to crush the ore coarse (about 1-inch), hydraulically separating the slime and treating the fines by spraying the pulp down a series of towers, countercurrent with SO_2 gas flow; the coarse ore was charged into percolation tanks with tight tops, the interstices between the ore lumps allowing easy upward passage of SO_2 gas through the charge. A fine spray of water or leach solution was added on top in quantity only sufficient to trickle through the charge and exit at the bottom. The second patent provided for a multiple series of shelves set staggered and filling the interior of a rectangular tank, the idea being to cover the shelves with fine ore charged at the top and to make the ore pass downward on the many shelves by vibration of each set. Steam and SO_2 were passed upward from the bottom and condensed leach liquor trickled downward through the charged apparatus. Both methods were tried at Ludwig, Nev., for leaching oxidized copper ores and were not commercially successful. The proposed methods offer less chance for success with the treatment of manganese ores.

United States Patent 1276739, as issued to C. Ellis, August 27, 1918, provides for leaching oxide manganese ores with acid-sodium sulphate to obtain manganese sulphate. His patent claim reads:

> A process for making manganese dioxide which comprises reacting on raw material containing basic manganese compounds with acid material comprising acid sodium sulphate at reacting temperature to form manganese sulphate and converting of this salt into manganese dioxide.

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G. D. van Arsdale and C. G. Maier obtained United States Patent 1304222 on May 20, 1919, for extracting manganese and making sulphuric acid and manganese dioxide. It consists in suspending ground manganese ore in water, adding acid to dissolve oxides of manganese other than dioxide, agitating and introducing sulphur dioxide gas into the pulp, and continuing to agitate while still conducting sulphur dioxide gas into the pulp until substantial completion of the reaction between the sulphur dioxide and the manganese compound contained in the ore, separating the resulting solution containing manganese from the leached ore residue, removing undesirable constituents of the solution, heating the manganese solution, and subjecting the heated manganese solution to electrolysis, making this electrolysis discontinuous as to the anode so as to produce desirable physical qualities in the separated manganese dioxide, continuing the electrolysis to attain a sufficient degree of purity and strength of the sulphuric acid produced and to obtain as dioxide enough of the manganese originally present, removing the substantially manganese free sulphuric acid thus produced, and in then removing the precipitated manganese dioxide from the anode.

The E. W. Haslup and B. A. Peacock process appears in United States Patents 1279108-10 of September 17, 1918, and 1291867 of January 21, 1919. It consists of treating a manganese ore with soluble sulphates, such as ferrous sulphate or aluminum sulphate, along with sulphuric acid of a gravity not more than 55° B., confining the ore mixture, devoid of added free water, for 15 hours or more in a closed receptable from which the heat of reaction is prevented from escaping until a temperature of 150° C. is reached and until the desired values have been transformed into sulphates, and then extracting the sulphates with water.

C. S. Vadner, under United States Patent 1188705, of June 27, 1916, and 1236236, of August 7, 1917, claims a process for the recovery of manganese and zinc from oxidized or roasted sulphide ores. He proposed spraying the pulp into sulphur dioxide gas for dissolution as sulphates. The resultant solution is oxidized by air, powdered limestone is added to precipitate the iron, then at elevated temperature fresh limestone is added to precipitate the zinc, and finally by the use of quicklime and air the manganese is precipitated as weldon mud. A latter improvement provides for passing the pregnant solution over manganese dioxide ore to precipitate the iron. Part of the large excess of readily soluble manganese united with all the remaining acid, and in this neutral solution iron is not held in solution. Vadner also proposes to leach the SO_2 residue with brine (sodium chloride) to dissolve the lead.

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Old Patents

Prof. E. H. Hersam gives the following review of old foreign processes for the treatment of manganese ores. They are of particular importance in showing the early development of hydrometallurgy of manganese.

In 1862 a process of ore treatment was patented in England by J. B. Readman, which consisted in fine-grinding the ore, mixing with sulphuric acid and sulphate of soda, drying, fusing, next adding lime and salt or bauxite, further igniting, and finally extracting with hot water, precipitating the sulphides of nickel and cobalt if present by sodium sulphide, evaporating the solution to crystallize the sodium sulphate, evaporating the mother liquor to dryness, and igniting in a muffle furnace with charcoal to produce the sulphide of manganese.

The Herrenschmidt and Constable process (British Patent 1555), which followed the above-described process, was devised in Australia. The treatment proposed, consisted in applying to the ores either warmed or at the ordinary temperature, a solution of the sulphate of iron which, as applied, reacts with oxides of manganese, and cobalt of the ore, produces the sulphate of these metals, and deposits the oxide of iron.

In 1884, appeared Readman's second English patent for a process of treating manganese ores. The process consists in pulverizing the ore, treating it with a solution of soluble chloride such as that of sodium, calcium, magnesium or iron, agitating with or without heat, and effecting the mixing in a furnace if desired. For the extraction of cobalt, iron chloride is preferred to the other chlorides, the desired amount being somewhat more than 1 part of the anhydrous chloride of iron to 1 part of ore. The mass, in any case, is heated to a temperature sufficient to decompose the iron chloride. The mass is then lixiviated with water to extract cobalt, nickel, and manganese and the very small amount of iron that dissolves.

A German patent (May 29, 1884) succeeding the one above-mentioned, was granted to R. Nithack for the injection of a spray of concentrated solution of the chlorides of these metals upon hot, inclined, fire clay tiles in an appliance provided for regenerating the chloride. By the action thus claimed the metal takes an oxygen, becomes a protoxide, and releases its chlorine, which is recovered in the form of hydrochloric acid for the further extraction.

In September of 1884, a patent was granted in England (No. 12044) to Herrenschmidt for an extension of his original process. The process aims chiefly towards the extraction of nickel but includes manganese and cobalt. For ore containing manganese, the material is ground and lixiviated hot with ferrous chloride, which results in the decomposition of the nickel, cobalt, and manganese minerals. The nickel and cobalt are precipitated from the solution by adding manganese sulphide or the hydrated oxide of manganese. The pure solution is either crystallized or evaporated to dryness to obtain hydrochloric acid and manganese oxide.

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Further improvements in the Herrenschmidt and Constable process appeared in 1885 (Dingler's polyt. Jour., vol. 252, p. 392), in which it was shown that, in the treatment of manganese and cobalt ores, it is best to boil with ferrous sulphate solution for a half hour, after which the clear solution may be decanted and the protosulphate of the metal oxidized to higher salts.

By a process devised by Campbell and Boyd (British patent 12426, June 24, 1893), the sulphate of manganese, in solution, obtained as a by-product in the manufacture of chlorine, is converted into a state of carbonate suitable for producing oxide by the Dunlop process. In this process the solution of sulphate is mixed with a solution of sodium carbonate, and the precipitated manganese carbonate is collected, washed, and treated by the Dunlop process for the production of the oxide. A modification of this method consists in running a manganese solution slowly into a solution of caustic soda, blowing air into the mixture the while, and continuing aeration for a time after neutrality is attained.

By a patented process of Albright and Hood (British patent 9271, May 1893), manganese ore is mixed with coal dust and sulphuric acid, after which it is heated on a furnace bed to produce manganese sulphate, which then is leached from the digested product. The solution of manganous sulphate is treated with calcium chloride, in excess, after which the precipitated calcium sulphate is separated. The washings are brought to a high state of concentration of the calcium chloride, lime is added and the solution is then treated with air in a Weldon oxidizer to produce the Weldon mud, a product before described. Another means of effecting this precipitation, that was suggested by these authors, was the use of ammonia as the precipitating agent. The excess of ammonia is recovered at the time of the oxidation of the precipitated manganese hydrate, and as sulphate by evaporation.

In 1894, A. R. Davis of Manchester patented (British patent 2696) a process of treating manganese peroxide with ferrous sulphate and separating the soluble sulphate of manganese from the iron thereby formed. The sulphate of manganese was to be used as such or to be evaporated for the production of the solid sulphate of manganese.

In 1895, Greene and Wahl (Dingler's polyt. Jour., 1895, vol. 296, pp. 112-114) prepared pure manganese, freed from iron, by crushing the ore, leaching the ore down to 0.1 percent with sulphuric acid in 2 to 3 volumes of water. By the treatment, the iron is extracted and the manganese dioxide remains unattacked. Their process included an extension of the treatment for the production of manganese free from carbon and iron, which consists in igniting the dioxide of manganese, heating to 400° to 500° C. to form Mn_3O_4, further reducing by the introduction of volatile hydrocarbons and finally in crucibles with aluminum or magnesium.

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CHAPTER 8. PYROMETALLURGICAL TREATMENT OF MANGANESE ORES

By T. L. Joseph[4]

PRODUCTION OF FERROMANGANESE

Reduction of Manganese Oxides

According to Meyer and Rötgers (256) heat alone will dissociate MnO_2 into Mn_2O_3 at 530° C. at atmospheric pressure. Manganic oxide (Mn_2O_3) is further dissociated into Mn_3O_4 at 940° C. under atmospheric pressure. Dissociation by heat alone is unimportant in blast-furnace practice, because reduction of the higher oxides occurs at temperatures below those required for thermal dissociation. Clevenger and Caron (50) found that the MnO_2 in a refractory silver ore was reduced to MnO in 2 hours at 465° C. in the presence of dry carbon monoxide. Nishibori (275) investigated the equilibrium conditions for the reaction

$$Mn_3O_4 + CO \rightleftharpoons 3MnO + CO_2$$

at 780° C. During the early stages of reduction virtually all of the carbon monoxide was converted to carbon dioxide. As the composition of the solid phase approached MnO the CO_2 in the gas phase decreased sharply from 100 to about 7 percent. These data show that gas with a $CO:CO_2$ ratio of 14:1, will reduce Mn_3O_4 to MnO at 780° C.

Reduction of Manganous Oxide

Several investigators have determined the temperature at which reduction of manganous oxide begins. Wüst (399) has reported the work of Meyer, who found that carbon monoxide will reduce this oxide of manganese in the presence of metallic iron at 1,150° C. Precautions were taken during reduction with CO to prevent carbon deposition. Reduction in the presence of solid carbon occurred at 1,100° C. Greenwood (124) has reported that reduction by retort carbon in the presence of electrolytic iron began at 1,030° C. and in the absence of iron at 1,105° C. He refers to metallic globules and to partial fusion of the metallic residue, which he separated from the unreduced oxide by treatment with sulphuric acid. Since metallic manganese melts at 1,244° C., it appears that his observed temperatures were lower than the true temperature. Royster (322, p. 119) states that laboratory tests strongly indicate that 1,265° C. is the lowest temperature at which MnO is reducible by carbon or carbon monoxide. The results of a single experiment reported by Nishibori (275, p. 296) indicate that reduction of Mn_3O_4 will progress beyond MnO at 780° C. in the presence of a gas phase consisting of 93.5 percent CO and 6.5 percent CO_2. The strong reducing action of the product of reduction towards sulphuric acid, a property not characteristic of MnO, was attributed to the presence of manganese or a suboxide of manganese.

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4 Metallurgist, U. S. Bureau of Mines.

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The results of these various investigators indicate that temperatures of 1,100° to 1,265° C. are necessary to reduce appreciable amounts of MnO in the presence of solid carbon and carbon monoxide.

Factors Controlling Amount of Carbon in Liquid Manganese Produced in the Presence of Carbon

Moissan (262) reduced Mn_3O_4 in the electric furnace in the presence of varying amounts of carbon. The fused metal produced in four experiments varied in percentage composition as follows:

	1	2	3	4
Mn	85.0	85.82	90.6	94.06
C	14.59	13.98	10.2	6.35

This variation in carbon content was attributed to the relative amounts of manganous oxide and carbon in the charge and to the temperature. In the presence of excess oxide fusions containing 4 to 5 percent carbon were obtained. When reduction was carried out at low temperatures, Moissan obtained metal as follows:

	1	2
Mn .... per cent	93.2	96.2
C .... do	4.5	3.6

Roberts and Wraight (316, p. 241) have also observed the effect of temperature upon the amount of carbon absorbed during reduction. They heated mixtures of pure Mn_3O_4 and powdered wood charcoal. When the estimated temperatures of reduction varied from 1,600° to 1,770° C. the proportion of carbon in the metal increased from 5.5 to 7.44 percent. Doubling the amount of reducing agent had little effect upon the amount of carbon absorbed by the metal.

Three tests were made by W. F. Holbrook and the writer to observe the amount of carbon that will dissolve manganese. In the first test a charge of C. P. manganese carbonate and finely divided charcoal was gradually heated to 1,900° C. Due to interference from fumes this temperature, observed with an optical pyrometer, is probably lower than the true temperature. The metal obtained consisted of small shot distributed throughout a mass of charcoal. Their carbon content ranged from 7.24 to 8.81 percent.

A smaller amount of charcoal was used in the second test, from which a slug of metal was obtained. The peak temperature observed was 1,900° C. Carbon determinations on portions of the piece of metal obtained varied from 7.97 to 8.52, averaging 8.22.

In the third test 30 grams of metal obtained from the two previous tests were heated in a graphite container closed at the top with a cone-shaped graphite rod. The object of this device was to hold the bath under some

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pressure, so that higher temperatures could be reached. During 47 minutes the temperature was gradually raised from 1,320° to 2,000° C. A clearer atmosphere in the furnace permitted more satisfactory readings than in the first two tests. At the end of the heating period the graphite plug was removed, and the graphite container was set in a steel cylinder surrounded by ice water. At the instant the graphite plug or cover was removed the metal boiled vigorously. A small round ingot, 5/8 inch by about 1 inch and weighing 27 grams, was recovered and sectioned for analysis. Various sections of the ingot contained the following percentages of carbon: 9.85, 10.00, 10.14, and 10.75, averaging 10.19.

Graphitic carbon determinations averaged 3.31 percent, leaving 6.88 percent combined carbon, which checks with the theoretical amount corresponding to the formula Mn_3C. It appears that the 3.31 percent graphitic carbon was either in solution as such or that the compound Mn_2C, which would correspond to about 10 percent carbon, broke down upon cooling.

Near the top of the ingot an irregular section was found to contain 11.36 percent carbon. This higher manganese content is attributed to contamination of the sample with graphite floating upon the surface of the melt. One could continue heating a melt of manganese until nothing but a residue of carbon remained; that is, as manganese is volatilized there might be an enrichment of mechanically held graphite. Such a condition could not account for the 3.31 percent graphitic carbon found in the third melt, because about 88 percent of the manganese charged was recovered.

Since Moissan's experiments were presumably conducted at about atmospheric pressure the manganese content (14.59 percent) appears to be due either to carburization in the solid state or to contamination of samples by a residue of mechanically held graphite. Whatever the mechanism of reduction may be, it appears that the absorption of carbon by liquid manganese is a function of temperature.

The experiments of Ruff and Bormann (328) indicate that a homogeneous liquid phase containing more than 7.12 percent manganese cannot exist at 30 mm pressure. Under this pressure the solution boiled at 1,526° C. Their work does not, however, indicate the amount of carbon that can be held in solution by liquid manganese at higher temperatures attainable at higher pressures.

Refining Action of Manganous Oxide upon Ferromanganese

The refining or decarburizing action of a slag rich in MnO has been studied by a number of investigators in connection with the problem of producing low-carbon ferromanganese, which is discussed on page 218. Roberts and Wraight (316, p. 281) reduced the carbon content of ferromanganese from 6.72 to 2.79 percent by heating it 3 hours under a semifused pasty mass of MnO at temperatures above 1,600° C. Humbert (173) has patented a method for reducing the carbon content of ferromanganese to about 1 percent or less by heating in the presence of manganous oxide at about 1,700° C. A similar method for decarburizing ferromanganese has been patented by Hadfield (134).

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Experimental evidence is not available to show definitely whether in high-temperature reduction liquid-manganese carbides are first formed and undergo subsequent refining in the presence of MnO or whether liquid metallic manganese is first formed and absorbs carbon in amounts depending upon the temperature and presence of oxides. Both reactions probably occur in the blast furnace.

Carburization of Manganese Produced in the Solid State

The reduction of MnO at temperatures below the melting point of manganese has received comparatively little attention. Reference has been made to Greenwood's (124) tests at reported temperatures of 1,030° to 1,105° C. The metallic residue, after separation from excess MnO, was treated with hydrochloric acid. From the composition of the gas evolved the carbon content was calculated to be 6 percent. The metallic residue had undergone partial fusion so that the carbon content may have been due to the combined effects of solution and the well-known reaction of case carburizing.

Muller and Barck (266) introduced a mixture of 43.3 cm^3 of carbon dioxide and 43.8 cm^3 of hydrogen over a sample of pulverized manganese and held the system at 800° C. until no further change in the volume of gas occurred (2 hours). The residual gas proved to be pure hydrogen and occupied a volume of 43.6 cm^3. The solid phase was identified as MnO and Mn_3C. The net result of the reaction may be expressed by the following equation

$$5\ Mn + CO_2 = 2MnO + Mn_3C.$$

Hilpert and Paunescu (163, p. 3479) heated finely divided manganese in a stream of methane and found that about 6 percent carbon was absorbed in an hour at 900° C. After 10 to 11 hours exposure at 900° C. the metal absorbed as much as 15 percent carbon. Carburization was much more rapid at 800° and at 900° C. than at lower temperatures less favorable to dissociation of methane into carbon and hydrogen. It is evident that under some conditions finely divided manganese carburizes very readily. In view of the readiness with which manganese carburizes it seems likely that if solid manganese is formed it would be converted very quickly by either CO or solid carbon to manganese carbide.

Reduction of Manganous Oxide in the Crucible of the Ferromanganese Furnace

One objective of good operating practice is to reduce the manganese in the slag to the lowest point consistent with fuel consumption and with tonnages that give the most economical operation. Crucible reactions are important because the manganese content of the slag tapped will depend upon the direction in which the crucible reactions are proceeding.

According to Wüst and Meyer (400), no reduction of manganese can occur below the tuyères in pig-iron furnaces because the slag is oxidizing toward the metal. Manganese equilibrium constants obtained from steel-making data were used to determine whether the slag tapped from a large number of pig-iron furnaces was oxidizing or reducing towards the metal produced. The manganese equilibrium values $K_{Mn} = \frac{MnO\ (slag) \times Fe\ (metal)}{FeO\ (slag) \times Mn\ (metal)}$, calculated from

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published blast-furnace data, were much smaller than values of K_{Mn} obtained from steel-making data. They concluded from this that slag from pig-iron furnaces is normally oxidizing toward the metal. Under such conditions no reduction of MnO, but rather oxidation of manganese, would occur below the tuyères if slag-metal reactions predominate over reduction of manganous oxide by carbon or by carbon monoxide.

The conclusion that manganese cannot be reduced below the tuyères of a pig-iron furnace is based upon three major assumptions: (1) Slag-metal reactions control the reduction of manganous oxide in the blast-furnace crucible in which there is a large excess of carbon existing as coke and carbon monoxide; (2) values of manganese equilibrium constants, obtained from steel-making data, can be applied rigorously to the crucible of a blast furnace; and (3) FeO normally reported in blast-furnace slag exists as such and not as metallic iron.

To determine whether manganese was reduced from slag which was oxidizing toward the metal the progress of the reduction of manganese from a mixture proportioned to produce ferromanganese and held at 1,550° C. was followed by a series of slag and metal samples. A charge of 275 grams of manganese ore, iron ore, and sufficient quantities of lime, alumina, and silica to produce about equal amounts of slag and metal was melted as rapidly as possible in a graphite crucible heated in an induction furnace. The melt was poured, cooled, and transferred to another graphite crucible for the reduction test. Charcoal was added as a reducing agent. The manganese and iron content of eight samples of slag and of metal, taken over a period of 2 hours after the slag was fused, are given in table 70. The same data are shown graphically in figure 26.

The small values of K_{Mn}, given in table 70, show that slag was very oxidizing to the metal throughout the whole period. Notwithstanding this fact, gradual reduction of manganous oxide occurred. The first metal sample contained 66.4 percent manganese and 25.85 percent iron. This metal was produced at 1,560° C. By applying the value of $K_{Mn} = 240$, reported by Körber (211) for this temperature, the ratio of MnO to FeO which must exist in the slag before reduction of manganese could occur by slag-metal reactions may be found as follows:

$$240 = \frac{MnO}{FeO} \times \frac{25.85}{66.4},$$

or

$$\frac{MnO}{FeO} = \frac{66.4 \times 240}{25.85} = 616.$$

Thus it may be seen that to produce metal containing 66.4 percent manganese by slag-metal reactions at 1,560° C. it would be necessary to have more than 600 times as much MnO as FeO in the slag. The production of such metal over a period when the ratio of MnO to FeO ranged from about 16 to 25 indicates the reaction between MnO in the slag and carbon or carbon monoxide, rather than slag-metal reactions, controls the reduction of manganous oxide under highly reducing conditions.

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TABLE 70. - Manganese and Iron in Slag and in Metal During Ferromanganese Reduction Test

Sample No.	Time after charge melted, minutes	Slag, percent		Metal, percent		$K_{Mn} = \frac{MnO\ (slag) \times Fe\ (metal)}{FeO\ (slag) \times Mn\ (metal)}$
		MnO	FeO	Mn	Fe	
1	0	60.0	3.68	....	.....	....
2	20	55.5	2.00	66.4	25.85	11.0
3	30	50.2	1.17	72.6	20.6	12.0
4	40	50.2	0.94	75.2	17.4	13.0
5	60	39.9	.25	81.0	11.8	23.0
6	75	30.0	.21	83.3	9.5	16.3
7	105	17.2	.36	83.8	9.0	4.5
Tap	125	11.25	.10	84.9	8.28	11.0

Tap slag, percent: SiO_2, 32.2; Al_2O_3, 9.05; CaO, 41.04.

Unless special precautions are taken to free slag samples from metallic shot, total iron determinations converted to a FeO basis have little significance. The slag samples reported in table 70 were cleaned of metal by grinding the slag and separating it into the following screen sizes: -100 +120, -120 +140, -140 +160, -160 +180, -180 +200, -200 + 270, -270 +400, -400. Each of the foregoing screen fractions was given a wet gravity separation. The heads from each sample were treated with a solution of copper sulphate and examined under the microscope before acceptance for analysis. Metal particles were copper-plated and therefore readily distinguished from the slag. In doubtful cases a microscopic count of the metal particles was made to be certain that contamination of the slag with iron from the metal would not exceed a few hundredths of 1 percent.

The experience gained in freeing these samples from metal leads one to believe that much of the iron reported in routine samples of blast-furnace slag occurs as metallic iron and not as FeO. It appears likely that the slags from pig-iron furnaces, considered by Wüst and Meyer, contained considerable metallic iron which was reported as FeO.

Another crucible test was made with a 300-gram charge to study the relative importance of slag-metal reactions and reduction of MnO by C or CO in the production of metal in the spiegeleisen range. The charge contained about three times as much manganese as iron and amounts of lime, alumina, and silica to yield a final slag of about the same composition as that produced in the ferromanganese reduction test.

Manganese equilibrium constants computed from the composition of metal shot and the slag from which they were recovered show that manganese was formed in the slag bath when the slag was oxidizing toward the metal. The data from this test are given in table 71.

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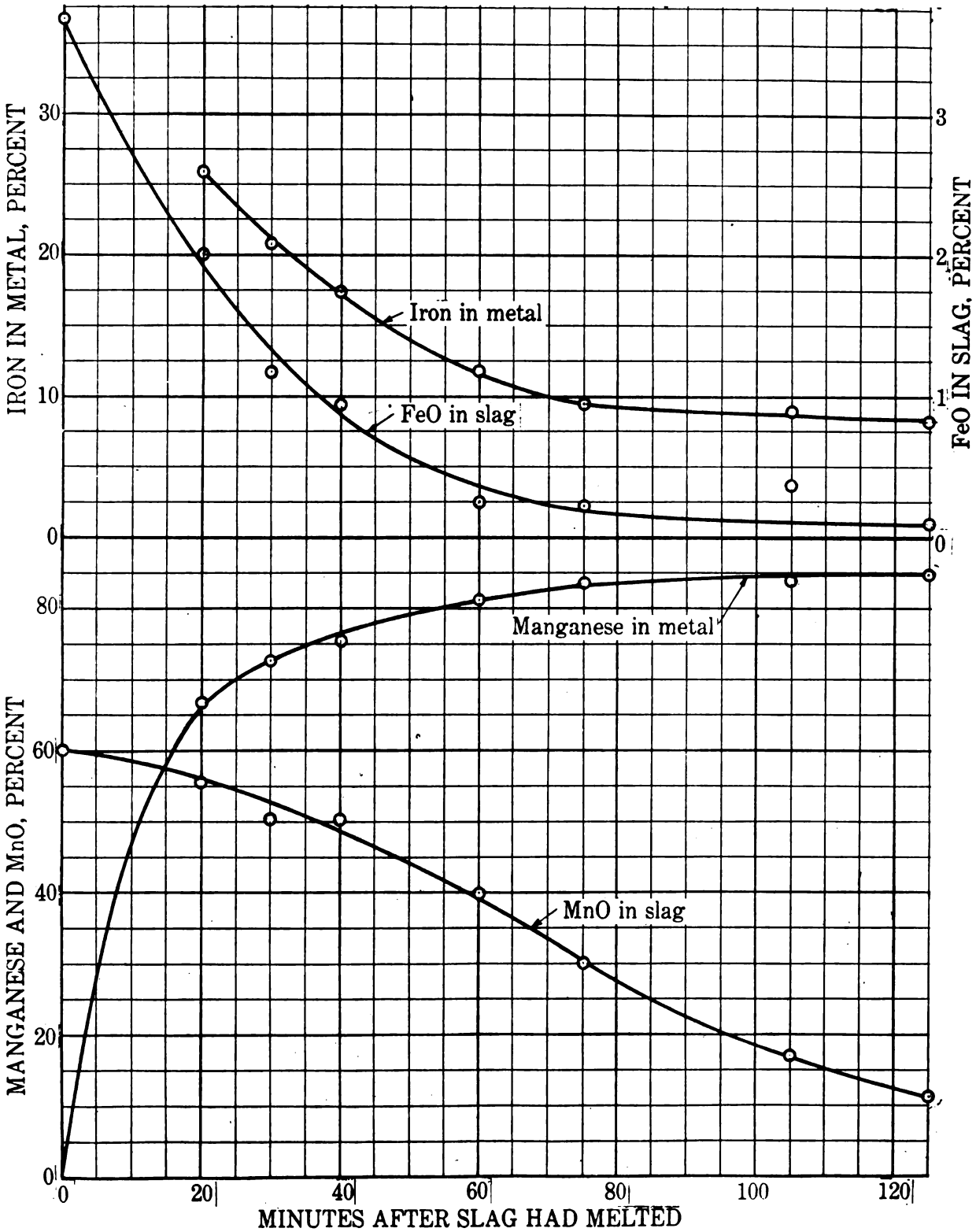

Figure 26.- Changes in slag and metal during ferromanganese reduction test.

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TABLE 71. - Changes in Composition of Slag and Metal During Spiegeleisen Reduction Test

Sample no.	Time after slag had melted, minutes	Metal shot removed from slag, percent		Bath metal, percent		Slag, percent		$K_{Mn} = \frac{MnO\ (slag) \times Fe\ (metal\ shot)}{FeO\ (slag) \times Mn\ (metal\ shot)}$	Temperature °C.
		Mn	Fe	Mn	Fe	MnO	FeO		
1	0	....	....	.....	....	29.2	9.32	...	1,553
2	20	15.0	81.0	5.13	89.0	33.0	1.57	110	1,535
	21								
	(Added 5 g. Fe_2O_3)								
3	40	....	....	10.90	83.0	29.1	.50	...	1,546
	41								
	(Added 5 g. Fe_2O_3)								
4	60	49.6	46.4	13.6	80.0	24.4	.41	56	1,535
	61								
	(Added 10 g. Fe_2O_3)								
5	80	49.5	46.5	....	....	21.7	.44	47	1,542
	81								
	(Added 10 g. Fe_2O_3)								
6	100	24.0	72.0	15.2	78.8	21.4	.49	131	1,530
	109								
	(Added 10 g. Fe_2O_3)								
7	114	23.6	72.4	....	....	23.9	2.29	32	1,535
8	130	....	....	16.0	78.0	....	....	...	
	138								
	(Added 10 g. Fe_2O_3)								
9	143	12.3	83.7	....	....	18.5	2.33	55	-
10	148	22.9	73.1	....	....	18.3	.89	65	-
11	153	21.6	74.4	....	....	16.4	.65	87	1,535
Tap	163	23.5	72.5	17.1	77.0	14.1	.31	139	-

Tap slag, percent: SiO_2, 32.74; CaO, 42.3; Al_2O_3, 9.64.

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It is well-known that the first metal produced from a mixture of the oxides of iron and manganese is higher in iron than metal produced later. Metal shot picked from the slag samples were used therefore to ascertain the composition of the metal produced during the various stages of reduction. These shot were invariably higher in manganese than the bath metal. The analyses of the shot and the bath metal are given in table 71. Small metal shot do not settle rapidly from a slag bath. They represent metal produced when the iron oxide in the slag was higher than at the instant the slag samples were taken. The slag was therefore more oxidizing toward the metal than the manganese equilibrium constants in table 71 indicate. The gradual decrease of manganese in the slag and the increase of manganese in the bath metal show that manganous oxide was reduced throughout the test. Ferric oxide was added from time to time to maintain a concentration of iron oxide in the slag readily determinable analytically and readily distinguishable from small amounts of metallic iron.

According to the concept that slag-metal reactions control the reduction of manganous oxide from slag and assuming that manganese equilibrium constants obtained from steel-making data can be applied to a system containing excess C and CO, slag 7 in table 71 should have contained about 80 times as much MnO as FeO to permit the forming of metal containing 23.6 percent manganese. Metal shot containing this concentration of manganese were actually formed in a slag containing only about 10 times as much MnO as FeO. The data, as a whole, point very definitely to the conclusion that reduction of MnO from slag in the presence of an excess of CO and C is not determined by slag-metal reactions but by those which follow:

$$MnO + C \longrightarrow Mn + CO,$$

or

$$MnO + CO \longrightarrow Mn + CO_2.$$

Concentrations of FeO necessary to oxidize manganese in the metal do not persist if the slag is fluid and a large excess of CO and C is present.

Wüst (399) observed that metal shot recovered from viscous slag were higher in manganese than the bath metal. He cited this result as evidence to support the view that manganous oxide is reduced above the tuyères and that no further reduction but oxidation of manganese occurs in the crucible below the tuyères. In this connection he states:

> There might exist the possibility that during retention of the washed iron (metal shot) in the slag, the silicon, manganese, and the phosphorus are reduced out of the slag by the carbide carbon of the iron. This conception is, however, negatived by the fact that so long as iron oxide is present in the slag in considerable quantity, a reduction of the above-mentioned oxides can not take place.

The presence of gas containing 34 percent CO and fractions of 1 percent CO_2 and the presence of a large excess of coke are not taken into consideration in the foregoing statement. One would expect the metal bath containing the first metal produced to be lower in manganese than metal shot formed within the slag after it has been partly depleted of iron oxide. Lumps of

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coke forced down into the slag bath below the inactive plastic core in the blast furnace no doubt act as nuclei around which metal reduced from the slag is formed. This phenomenon was shown by small particles of metal-coated charcoal found in samples taken during the crucible tests previously described.

Tests Showing Manganese is Reduced Below Tuyères. - The results from crucible tests indicating that reduction of manganous oxide below the tuyères is largely controlled by reaction with C or CO, and not by slag-metal reactions, is borne out by the manganese content of liquid metal samples removed from the crucible of pig-iron furnaces. Bansen (14) has reported average analyses of metal samples removed from the lower part of a pig-iron furnace as follows:

Sampling level	Composition of metal, percent			
	C	Si	Mn	P
6 ft. 9 in. above main tuyères	1.32	1.86	0.66	0.58
Main tuyère level	2.81	1.33	.86	1.03
33.5 inches below tuyères	4.06	2.05	1.55	1.79
Tapped metal	3.64	.45	1.58	1.80

The above analyses show that metal from the tuyère level contained about one half as much manganese as the tapped metal and metal removed from a slag notch. Analysis of partly reduced ore taken from the slag notch during this investigation indicates that manganese was reduced when the slag was very oxidizing towards the metal according to manganese equilibrium constants obtained from steel-making conditions. The reduction of manganous oxide under such conditions shows that, except for periods of hanging and slipping when unusually large amounts of unreduced oxides may be brought into the crucible, slag-metal reactions play a minor part in the reduction of manganous oxide below the tuyeres.

Mund, Stoecker, and Eilender (267) removed 600 liquid samples and 150 gas samples from a blast furnace across four levels as follows: Auxiliary tuyères, 6 feet above the main tuyères; main tuyères; main slag notch, 3.2 feet above the hearth; and auxiliary slag notch, 4.5 feet above the hearth. The analyses of the metal samples taken were correlated with the analyses of 300 samples of pig iron. Samples were taken through plugged and through normally-working tuyères. The manganese content of the metal samples removed from the auxiliary tuyères was about two thirds that of the tapped metal. In front of both the auxiliary and main tuyères a strong oxidation of manganese occurred, particularly in the oxidizing portions of the combustion zones that extended about 32 inches beyond the nose of the tuyères. From about 32 to 48 inches from the nose of the tuyères the manganese increased rapidly and at the latter position approached the manganese content of the tapped pig iron. Beyond this position the manganese content decreased, presumably due to a decrease in the temperature prevailing in the central part of the idle core or what the German investigators have called the "stille Mann." It would appear that more metal moves down through the periphery than through the central inactive core. Samples drawn from sections of the periphery were therefore more representative

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of the metal passing any particular plane. In view of the oxidation of manganese in the combustion zones, it is evident that a large amount of manganese was formed below the tuyères. The increase in the manganese in the metal between normally working tuyères and the slag notch also shows very clearly that a great deal of manganous oxide is reduced below the tuyères. Tapped metal was higher in manganese than that removed from the slag notch, indicating that a considerable amount of manganous oxide was reduced from the slag layer adjacent to the metal bath.

No direct information, similar to that obtained on pig-iron furnaces, is available on the conditions in a ferromanganese furnace. The gas samples removed by Perrott and Kinney (300) from the tuyères of a furnace producing ferromanganese show, however, a decided deficiency of oxygen up to a position about 32 inches from the nose of the tuyères. From the converter process for making steel one would expect that the major part of this oxygen is removed from the gas phase by the oxidation of the manganese which is again reduced in the crucible.

Inactive Zone in Bosh and Crucible. - A picture of the conditions existing in the crucible of a blast furnace is essential in obtaining an understanding of crucible reactions. The investigations of Ebelmen, Van Vlcten, Perrott and Kinney, and Lennings have definitely established the existence of localized combustion zones in front of the tuyères. In formulating a conception of the effect of these localized zones upon stock flow in the furnace, it appeared to Royster and the writer (323) that a central area of the furnace at the tuyère level is comparatively inactive. Stoecker (357) concluded from explorations of the hearth and bosh that this inactive zone (or dead man) begins above the main tuyère level, at which it was roughly 6 feet in diameter. At this level it consists of unreduced ore and coke. Below the tuyeres it widens and rests on the hearth. At the bottom it consists of coke, only. The dimensions of this inactive core and its permeability vary depending upon the diameter of the hearth and the amount of coke used per ton of iron.

In observing the rate of stock descent in various parts of the furnace, Kinney (206) observed a pendulumlike movement of the stock column during charging, indicating that the lower part of the stock column was supported by a fluid. If one considers the volume occupied by the metal and slag previous to a metal cast, it becomes obvious that only a part of the volume available below the tuyères is occupied by slag and metal. It appears therefore that a core of plastic material, extending below the tuyère, and coke, submerged in the liquid bath, occupy a considerable portion of the crucible. Whether the inactive core rests on the hearth would, it appears, depend upon the depth of the metal layer and the upward pressure exerted by the blast of air applied through the tuyères.

Kinney (207) observed a temperature of 1,250° C. in the center of a 300-ton foundry furnace having a hearth diameter of 14 feet 6 inches, compared to a tuyère temperature of 1,534° C. Rheinlander (313) has also observed that the center of the furnace is comparatively cold. He states that, although the temperature can not be rigidly established, about 4.5 feet beyond the tuyères it is under 1,500° C. In the central part of the core the temperature varied between 1,000° and 1,100° C.

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Although there is no direct information about the existence of a comparatively cold inactive zone in the central part of the crucibles of ferromanganese furnaces it seems quite certain that such an idle core exists in some modified form. In the ferromanganese furnace, as in pig-iron furnaces, the major part of the metal passes through the oxidizing atmosphere in front of the tuyères. Manganous oxide so formed is reduced from the slag surrounding this inactive core and to some extent within the core itself. The low temperature in the central area does not, however, favor manganese reduction. Metal high in manganese may be found in this central core, but it is a minor part of the total metal produced. The final reduction of manganous oxide, which has a pronounced effect upon the manganese carried out in the slag, occurs in the slag layer, which contains coke forced into the slag by the overlying stock column. This layer of slag, in which the temperature is maintained by convection, is hotter than the central core through which heat is transmitted largely by conduction. Coke thus submerged in the slag forms strongly reducing areas. The coke is also effective in maintaining a gas phase consisting of about 34 percent CO and fractions of 1 percent CO_2, the balance being largely nitrogen.

Melting Points of Manganese Silicates

The extent to which MnO can be reduced without fusion depends upon its purity, particularly with respect to silica. Manganous oxide melts at approximately 1,600° C. and can therefore be reduced without fusion. Dörinckel (73) has studied the system $MnO-SiO_2$. According to his equilibrium diagram, tephroite ($2MnO.SiO_2$, 29.8 weight-percent SiO_2) solidified at 1,323° C. and rhodonite ($MnO.SiO_2$, 45.9 weight-percent SiO_2) freezes at 1,230° C. A eutectic between these two silicates, containing 41 percent SiO_2 by weight, solidifies at 1,190° C. Herty, Conley, and Royer (158), who have recently studied this same system, report somewhat higher melting temperatures for corresponding points in the equilibrium diagram.

Figure 27, from the report of Herty, Conley, and Royer, contains the ternary diagram for the system $FeO \cdot MnO \cdot SiO_2$ and the binary diagrams for the systems $FeO \cdot SiO_2$, $MnO \cdot SiO_2$, and MnO·FeO. For present consideration, the binary system $MnO \cdot SiO_2$ and that portion of the ternary system adjacent to it have primary importance. The major part of the oxygen combined with the iron in manganese ores is probably removed before fusion temperatures are reached. Higher oxides of manganese are reduced to manganous oxide. By the time the particle reaches fusing temperatures manganous oxide and silica are the major constituents of ores in which the gangue is chiefly silica. Fusing temperatures will depend upon the proportions of silica and manganous oxide present and will range from about 1,600° C. for pure manganous oxide to 1,250° to 1,350° C. in the range of 30 to 40 percent silica.

Incomplete reduction of ferrous oxide (due to lack of time, size of ore particle, or low permeability to reducing gases) would tend to lower the melting points of the ore particle undergoing reduction. Herty, Conley, and Royer have determined the melting points of slags whose compositions are indicated by the circles in the ternary diagram of figure 27. A melting temperature of 1,320° C. has been reported for a slag containing 9.01 percent FeO,

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83.6 percent MnO, and 7.39 percent SiO_2. If such a three-component slag were converted to a two-component slag by reduction of the ferrous oxide the melting point would be increased to about 1,540° C. Ferrous oxide has less effect in lowering the melting temperature in the range of higher-silica content. If a three-component slag composed of 12.42 percent FeO, 72.74 percent MnO, and 14.84 percent SiO_2, with a melting point of 1,310° C. is converted to a two-component slag by reduction of ferrous oxide, the melting point would increase to 1,475° C. Thus it may be seen that incomplete reduction of ferrous oxide would promote the formation of liquid silicates and tend to minimize reduction in the solid state.

Many commercial ores contain about 8 percent silica and 50 percent manganese. After the higher oxides of manganese and the iron minerals are reduced, the remaining portion of such material would contain about 90 percent manganous oxide and 10 percent silica and would have a melting temperature of 1,475° to 1,500° C. Before such temperatures are reached, however, reduction of manganous oxide occurs along the periphery of the ore particles. As reduction proceeds the ratio of silica to manganese increases until it reaches a point at which the outer shell first softens and finally melts. The manganese silicates so produced subsequently combine with the calcium oxide and magnesium oxide. These basic oxides would be absorbed in the initial slag formed at points of direct contact between the lumps of ore and calcined limestone. The effect of the calcium oxide in retarding the formation of manganese silicates and in raising the free-running temperature of the slag tends to increase hearth temperatures.

A more siliceous manganese ore containing, for example, 15 percent silica and 45 percent manganese, would contain about 80 percent manganous oxide and 20 percent silica after the higher oxides of manganese and the iron minerals had been reduced. This material would melt at about 1,450° C. which is in the temperature range required for rapid reduction of manganous oxide. Reduction of comparatively small amounts of manganous oxide along the outer surface of the piece would concentrate the silica to a point that would permit softening and fusion. Thus it may be seen that silica in the ore promotes the formation of manganese silicates and tends to minimize the amount of manganous oxide reduced prior to fusion. After the slag is formed high silica in the charge results in a dilution of manganous oxide in the slag. In addition to the dilution due to silica, there is further dilution as a result of the calcium oxide used to flux the silica.

It appears from data obtained on pig-iron furnaces that some reduction of manganous oxide occurs before fusion. Part of the manganese reduced above the tuyères is oxidized in passing through the combustion zones. Final reduction in the crucible, which governs the loss of manganese in the slag, is very important. Adjustments in fuel requirements, in the blast temperature, in the speed of driving, and in slag basicity, together with the selection of raw materials of low-silica content are of foremost importance in minimizing the loss of manganese in the slag.

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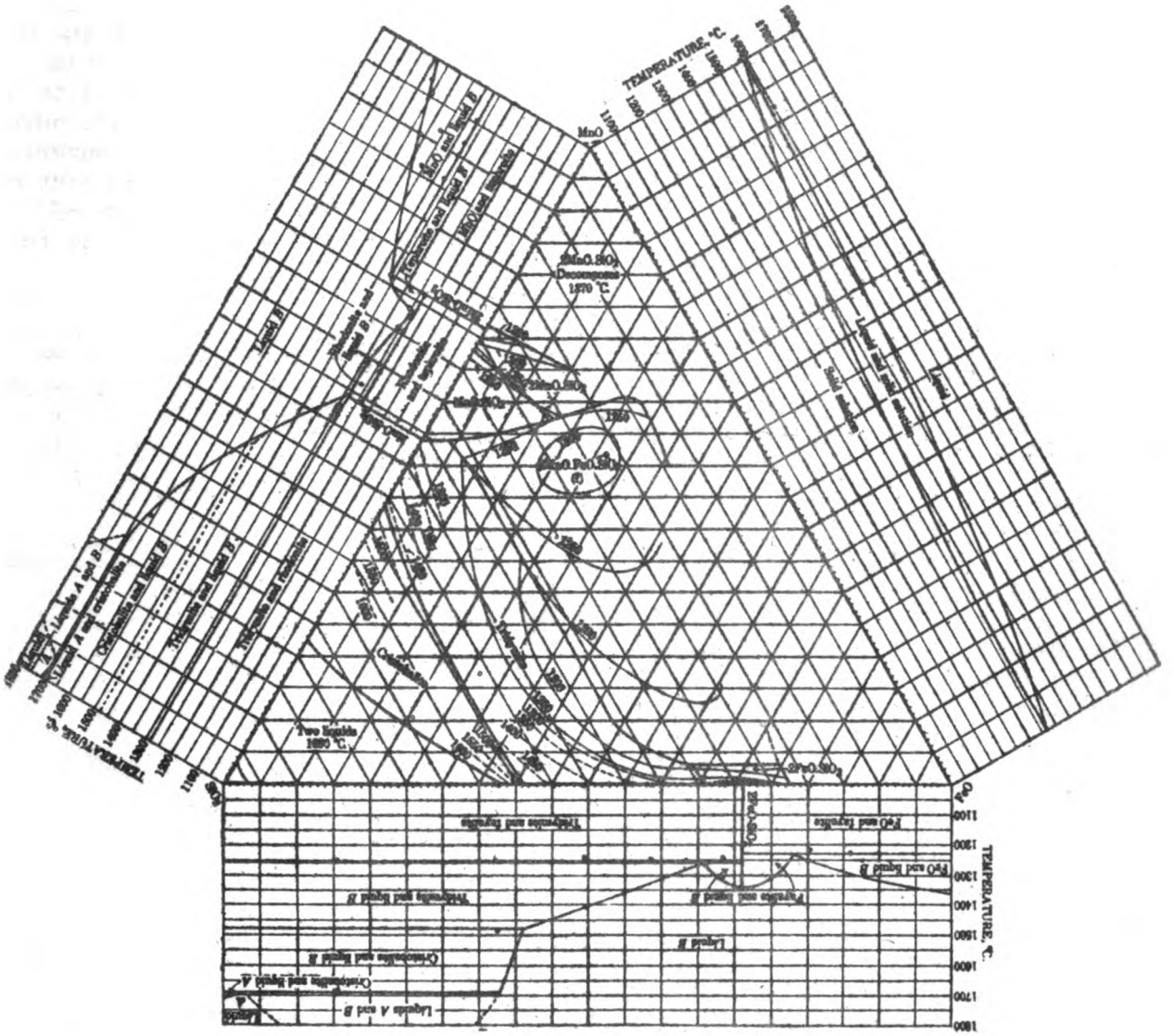
TEMPERATURE, °C.
MnO
2MnO.SiO2
Decomposes
1270 °C.
Two liquids
1680 °C.
Liquid B
Tridymite and liquid B
Cristobalite and liquid B
Tridymite and Fayalite
Fayalite and liquid B
FeO and liquid B
Liquid A and B
Liquid B
Solid solution
Liquid and solid solution
Solid solutions
Cristobalite and liquid A
Tridymite and liquid A
Cristobalite and Fayalite
Tridymite and Fayalite
FeO and Fayalite
Liquid A and B
Cristobalite and liquid A
Tridymite and liquid A
Cristobalite and Fayalite
Tridymite and Fayalite
FeO and Fayalite
Liquid B
Fayalite and liquid B
FeO and liquid B

Reduction of Manganese from Slag

Christianson and Hunter (48) obtained data on the reduction of manganous oxide in an investigation of the Jones process. Samples of manganiferous iron ore (10 to 24 percent manganese, 24 to 40 percent iron, and 10 to 26 percent silica) were mixed with coal and heated in graphite crucibles for 30 to 40 minutes at 1,250° to 1,300° C. About 93 percent of the iron and 2 percent of the manganese were reduced and entered the metal, which averaged 94.2 percent iron and 1.0 percent manganese. At the end of the test the entire content of the crucible was poured, the metal being recovered as a button. A partial analysis of the slag was as follows: 5 percent iron, 29 percent manganese, and 31 percent silica. These tests show that manganese silicates are slowly reduced below 1,300° C.

A series of reduction tests was made at higher temperatures on the manganese slag produced, as indicated above, from ferruginous manganese ores. The slag was crushed to minus 30-mesh, mixed with coke and limestone, and heated in hollow carbon electrodes. It was necessary to raise the temperature to about 1,450° C. before rapid reduction took place. Below 1,450° C. the reaction was so slow that little metal was produced.

Thermal Principles

The total heat absorbed by the two reactions,

$$MnO + CO = Mn + CO_2, \quad -41,148 \text{ B. t. u.},$$
$$CO + C = 2CO, \quad -59,984 \text{ B. t. u.},$$

is the same as the heat absorbed by the reaction,

$$MnO + C = Mn + CO, \quad -111,132 \text{ B. t. u.}$$

That is, whether MnO is reduced by C or CO the reduction of each formula weight of manganese requires 111,132 B. t. u. or 2,020 B. t. u. per pound of manganese. Thus it may be seen that the reduction of MnO is very different thermally from the reduction of FeO, from which a pound of iron can be produced with a gain of 75 B. t. u. (If manganous oxide is reduced to manganese carbide, the reaction is slightly less endothermic; 1,920 B. t. u. per pound of manganese as the carbide).

Distribution of Heat in Pig-Iron and Ferromanganese Furnace

A comparison between heat balances of pig-iron and ferromanganese furnaces shows why it requires less than one half as much coke to produce a ton of pig iron as it does to produce a ton of ferromanganese. Data in table 72 on the distribution of heat in pig-iron furnaces were taken from average values obtained by Royster, Kinney, and Joseph (324) for 14 American pig-iron furnaces. The heat balance for a ferromanganese furnace was calculated by Clements (49).

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TABLE 72. - Distribution of Heat in Blast Furnaces Producing Ferromanganese and Pig Iron

Heat generated

B.t.u. generated per ton	Pig iron,1/ 15,270,800	Ferro-manganese2/, 24,470,000
	Percent	Percent
Combustion of C to CO_2	52.19	22.38
Combustion of C to CO	34.12	55.59
Heat in blast, including moisture	13.69	19.46
Heat generated by formation of silicates	-----	1.65
Heat generated by formation of carbides	-----	.92
Total	100.00	100.00

Heat consumed

Reduction of ferric oxide	42.92	3.57
Reduction of manganese oxides, phosphorus pentoxide, and silica	3.44	29.96
Dissociation of calcium carbonate	4.53	4.94
Dissociation of moisture	7.30	7.44
Carried off with metal	7.50	6.42
Carried off with slag	6.08	7.83
Carried off with dry gases	6.05	21.30
Carried off with moisture in top gas	4.15	2.97
Dissociation of manganese silicate	-----	.07
Dissociation of manganese hydroxide	-----	.82
Decomposition of calcium phosphate	-----	.11
Formation of calcium sulphide	-----	.81
Heat in flue dust	-----	.20
Heat absorbed by blast expansion	-----	.42
Heat in cooling water and radiation losses	18.03	13.14
Total	100.00	100.00

1/ Average data on 14 American blast furnaces reported by Royster, Joseph, and Kinney.
2/ Heat balance on a blast furnace by Clements.

Heat generated

Table 72 shows that 52.19 percent of the heat generated in the pig-iron furnaces was derived from combustion of C to CO_2, while in the ferro furnace only 22.38 percent of the heat was derived by combustion of C to CO_2. More than half the heat generated in the ferromanganese furnace was obtained by combustion of C to CO. The production of 1 ton of ferromanganese required 3,700 pounds of fixed carbon, from which 18,078,192 B. t. u. were generated, whereas the production of 1 ton of pig iron required approximately 1,700

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pounds of fixed carbon, from which 13,179,300 B. t. u. were produced. These figures do not include the heat in the hot air used for combustion. In the ferromanganese furnaces, 4,885 B. t. u. were generated per pound of fixed carbon in the coke compared to a similar figure of 7,740 B. t. u. for the pig-iron furnaces. Thus it can be seen that about 1.6 times as much heat is generated per pound of carbon in the pig-iron furnaces. The production of a ton of ferromanganese on 3,700 pounds of fixed carbon is good practice, whereas the production of a ton of pig iron on 1,700 pounds of fixed carbon does not represent the best practice.

Johnson (180) states that maximum blast-furnace fuel economy depends (1) upon the development of the maximum possible amount of heat from each pound of fuel and (2) a certain irreducible proportion of the heat generated should be developed above the free-running temperature of the slag. The ferromanganese furnace violates both of these principles of fuel economy. The operation is characterized by high percentages of CO in the top gas because this gas is the end product of MnO reduction. The second principle of fuel efficiency enunciated by Johnson is based upon the desirability of maintaining hearth temperatures at which reactions that occur in this part of the furnace will go forward rapidly. In the pig-iron furnace the important hearth reactions are reduction of silica and desulphurization of the iron. High hearth temperature, which implies high temperatures of the tuyères, of the slag, and of the metal, would be very desirable in a ferromanganese furnace. In spite of the large amount of fuel used these temperatures in ferromanganese furnaces are low in comparison with those in pig-iron furnaces, as may be seen in table 73.

TABLE 73. - Hearth Temperatures

Furnace	Temperatures, ° C.		
	Tuyères	Slag	Metal
Foundry iron	1,748	1,553	1,493
Bessemer iron	1,733	1,513	1,466
Basic iron	1,669	1,522	1,468
Charcoal	1,669	1,451	1,415
Ferromanganese	1,550	1,426	1,386
Spiegeleisen	1,597	1,427	1,392

The average temperatures of the pig-iron furnaces are: Tuyères, 1,717° C.; slag, 1,529° C.; and metal, 1,476° C. Similar average values for ferromanganese furnaces are: 1,550°, 1,426°, and 1,386° C., respectively. Two factors are largely responsible for the lower temperatures in the ferromanganese furnaces. It has been pointed out that the reduction of MnO, whether by solid C or by CO, is highly endothermic. The absorption of heat in the lower part of the bosh, in the tuyère zone, and in the slag below the tuyères tends to lower what has been loosely called the hearth temperature. Slag, which is formed at low temperatures and which is fluid at temperatures just above its melting point, carries a comparatively small amount of heat into the crucible of the furnace. Less heat is absorbed above the fusion zone by the slag constituents. After fusion the slag passes rapidly over the coke lumps and absorbs a small amount

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of heat in the bosh. Upon reaching the tuyère zone the large thermal head between the comparatively cold slag and the tuyères has a chilling effect upon the combustion zone. The net result is that the slag reaches the crucible at low temperatures. The temperature of the metal is governed largely by the temperatures of the tuyères and of the slag. This may be seen from the slag and metal temperatures reported in table 73. The slag has the predominating influence. Since the region of the furnace below the tuyères depends largely upon the slag and metal for its supply of heat, cold slag and cold metal mean comparatively cold temperatures in the crucible. Thus it may be seen that the low free-running temperature of the slag in ferromanganese and spiegel furnaces is not conducive to the high temperatures required for reduction of MnO. Since the temperature does not aid rapid reduction the alternative is to allow a longer time by bringing fresh slag from the bosh into the crucible at a slower rate.

Heat Consumed

Heat requirements for the calcination of carbonates and the dissociation of moisture are about the same in ferromanganese and pig-iron furnaces. The amount of heat carried off with the slag and metal is also about the same in the two types of furnaces. About 2.5 times as much heat is carried off with the exit gases from the ferromanganese furnace. This is the direct result of high top temperatures in the ferromanganese furnace and the larger volumes of exit gases per ton of metal produced. The volume of exit gases varies approximately as the fuel consumed per ton of metal, that is, from 2.5 to 5 times as much gas is produced in making 1 ton of ferromanganese. High top temperatures in ferromanganese furnaces are due to the small heat capacity of the charge. Furnas (103) found that the transfer of heat from gases to beds of broken solids depends upon the heat capacity of the bed per unit of volume. The specific heat of the ore and coke do not differ widely, both being on the order of 0.25. The weight of 1 cubic foot of stock in a pig-iron furnace is about 50 percent greater than in a ferromanganese furnace. This increase of 50 percent in heat capacity per unit volume of the charge permits more efficient acquisition of heat from the gas stream by the solids in pig-iron furnaces. Due to less efficient transfer of heat from the rising gas stream to the descending stock in the ferromanganese furnace the temperature of the top gas will range from 700° to 900° F. compared to 275° to 450° F. for pig-iron furnaces. Heat balances (table 72) for the two types of furnaces show that 3 to 4 times as much heat per ton of metal is carried off in the dry top gases issuing from the ferromanganese furnace.

Raw Materials for the Production of Ferromanganese

Ore

No rigid specifications can be set up for ores which may be used in producing ferromanganese because the value and feasibility of using a particular ore depend upon its cost and grade and the cost of other ores available at a specific point. The ore mixture usually consists of a number of ores, the proportion of each being regulated to meet rather definite chemical specifications for the over-all mixture. By blending a number of ores it is also possible to improve the physical character of the charge.

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The proper ratio of manganese to iron is a foremost requirement of the ore burden. Standard ferromanganese averages 80 percent manganese and about 12.5 percent iron, a ratio of manganese to iron of 6.4 to 1. If no iron were obtained from the coke, a ratio of manganese to iron of 8 to 1 in the ore burden would be satisfactory if 80 percent of the manganese were recovered ($\frac{6.4}{0.8} = 8$). According to a careful chemical balance which Clements made from average data covering 2 weeks operation of a British furnace, about 25 percent of the total iron charged was derived from the coke (table 74). Only about 87 percent of the iron charged appeared in the alloy. The amount of iron derived from the coke will obviously vary with the fuel consumption and with the amount of iron in the coke ash. In general, the charge, including the coke, will contain 6 to 7 times as much manganese as iron. Allowing for a loss of 20 percent manganese and considering the iron obtained from the coke, the ore mixture should contain from 9 to 10 times as much manganese as iron.

Newton (274) has shown that the approximate grade of alloy can be calculated from the percentage of manganese and iron in the ore and from the recovery of manganese. Ferromanganese contains about 80 percent of manganese and 12 percent of iron. The percent manganese in the alloy may therefore be calculated as follows:

$$\text{Percent Mn in alloy} = \frac{(\text{percent Mn in ore} \times \text{recovery of Mn}) \times 0.92}{(\text{percent Mn in ore} \times \text{recovery of Mn}) + \text{percent Fe in ore}}.$$

The application of the formula to an ore containing 49.5 percent Mn and 5.5 percent Fe, smelted with a recovery of 80 percent Mn, may be illustrated as follows:

$$\frac{(49.5 \times 0.80) \times 0.92}{(49.5 \times 0.80) + 5.5} = 81.0.$$

Thus it may be seen that according to this formula an ore mixture containing nine times as much manganese as iron will yield an alloy containing 81 percent manganese. If the amount of iron in the coke is increased 20 percent due to iron obtained from the coke, an alloy containing 79 percent manganese would be produced.

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Silica Penalty

Ores low in silica are preferable for producing manganese alloys because the volume of slag increases as the silica in the charge increases. Increased slag means large losses of manganese, increased fuel, and loss of tonnage. From a study of data on furnaces operated during the War, Royster (322, p. 126) obtained a figure of 0.88 pound of carbon for each additional pound of slag. Newton assumed that 0.3 pound of carbon would be required to melt 1 pound of slag. The latter figure is a little higher than the theoretical values obtained by Evans and Bailey Scott, Deladriere, Lilot, Clements, and Johnson. These values have been averaged by Mott and Wheeler (264). These theoretical values are based upon the assumption that all the carbon charged is used in generating heat. This assumes that no carbon is involved in the reduction of manganese by endothermic reactions. The figure by Royster, based upon domestic practice with siliceous ores during 1917 and 1918, may be high for slag values ranging from 1,500 to 2,500 pounds but should be fairly accurate for higher slag volumes.

All important considerations, such as extra coke, extra flux, slower production, and higher costs above raw materials, are reflected in the price schedule (384) of ferromanganese ores which was adopted by the ferro-alloys committee of the American Iron and Steel Institute and was also approved by the War Industries Board in 1918. For each percent of silica in excess of 8 percent and up to and including 15 percent, the penalty was 50 cents per ton; between 15 and 20 percent silica, the penalty was 75 cents per ton. Langhorne (229) calculated the cost of producing 1 ton of ferromanganese from two ores containing 14.25 and 14.32 percent silica. The theoretical cost of producing 1 ton of ferromanganese from siliceous ore showed an increase of about $10, assuming that a unit of manganese cost 60 cents in both cases. Since this additional cost would be distributed over about 2 tons of ore, it indicates a penalty of 50 cents per unit of silica in the ore.

Phosphorus

The amount of phosphorus in ferromanganese is governed almost entirely by the phosphorus content of the charge. Whether justifiable or not, the upper limit set by the trade for phosphorus in standard ferromanganese is 0.3 percent, which means that the ore mixture should average about one half of this or less. If the phosphorus in an ore exceeds 0.2 percent, there is considerably less freedom in the selection of other ores. The amount of phosphorus in the coke and flux must also be considered. A phosphorus penalty, adopted in 1918 by the ferromanganese committee of the American Iron and Steel Institute and approved by the War Industries Board, was as follows:

> For each 0.01 percent in excess of 0.25 percent phosphorus there shall be a penalty against unit price paid for manganese of one-half cent per unit figured to fractions.
>
> In view of existing conditions, and for the purpose of stimulating production of domestic manganese ores, there will be no penalty for phosphorus so long as the ore shipped can be used to advantage by the buyer. The buyer reserves the right to penalize excess phosphorus as above by giving 60 days' notice to the shipper.

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The above prices to be net to the producer; any expense, such as salary or commission to buyers' agent, to be paid to the buyer.

Settlements to be based on analysis of ore sample dried at 212° F. The percentage of moisture in ore samples as taken to be deducted from the weight.

During the period 1911 to 1929 about 14 pounds of metallic manganese were used to produce 1 ton of steel. This is equivalent to 17.5 pounds of standard 80 percent ferromanganese. The addition of 17.5 pounds of ferromanganese, containing 0.3 percent phosphorus, to 1 ton of steel would increase the phosphorus by 0.0023 percent. Ingot samples often show a larger increase than this over samples taken before the addition of ferromanganese to the ladle because a small amount of phosphorus is reduced from the slag by carburizing agents. Herty (149) states that trebling the amount of phosphorus commonly found in ferromanganese and spiegel would not bother the steelmaker.

Physical Structure of Ores

The importance of physical structure is recognized in buying manganese ores. Hard, coarse ores are purchased for mixing with fine ores to curtail dust losses. A portion of the dust is recovered and charged in the raw form or briquetted. There is, however, an economic loss of manganese and an aggravation of troubles due to dust deposition in stoves and boilers.

The physical character of the ore is not important from the standpoint of resistance to gas flow, as the existing quantity of coarse coke results in a porous column offering little resistance to gas flow. Fine particles in the ore as charged or produced in the furnace make it difficult, however, to obtain uniform distribution of the gas, a matter very closely connected with the efficiency of the furnace as a heat interchanger between gases and solids. The physical character of the ore used in pig-iron furnaces places a limit upon tonnages; that is, a point is reached at which the pressure developed in the furnace interferes with the travel of the stock. This is not true of furnaces producing ferromanganese because recovery of manganese from the slag is the factor limiting the rate of blowing.

Coke

Low ash content is of foremost importance in selecting coke for use in furnaces producing ferromanganese because, in addition to higher fuel requirements and decreased tonnages, coke ash leads to an economic loss of manganese in the slag. With a consumption of 4,500 to 6,000 pounds of coke per ton of ferromanganese each percent increase in coke ash will result in an increase of about 100 pounds of slag. The harmful effects move in a vicious cycle. Increased ash lowers the fixed carbon in the coke, making more coke necessary, which, in turn, introduces more ash, requiring more coke.

It has been pointed out that in the range of 10 to 15 percent SiO_2, each additional percent in the ore adds about $1 to the cost of producing 1 ton of ferromanganese. Silica in the coke is more harmful than silica in the ore, because in addition to increasing the volume of slag it also replaces fixed carbon.

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Coke with a low bulk density in the furnace is very desirable because this implies that the coke is strong yet porous and contains a limited amount of small sizes. Such coke, in addition to having thermal advantages, also has the advantage of producing a charge more permeable to gas flow.

Mott and Wheeler (264, p. 149) have summarized the most important properties of blast-furnace coke in the First Technical Report of the Midland Coke Research Committee, as follows:

> From this survey of the more obvious chemical and physical properties of cokes it is evident that the most important are: Moisture and ash contents, hardness, and size. The value of a coke for blast-furnace use can be improved by decreasing the amounts of moisture and ash it contains, by increasing the hardness and by eliminating breeze.

In ferromanganese practice the attainment of high temperatures in the combustion zones is very important. In this connection these investigators state:

> It is not possible at present to specify that property of a coke on which the attainment of high temperatures of combustion depends. Apparently the harder cokes yield the higher temperatures, whilst the size of the coke pieces is of importance.

The over-all rate of combustion of coke depends largely upon the rate at which air is supplied. Large sizes of less reactive coke that promote high concentrations of CO_2 by retarding the endothermic reaction between carbon and carbon dioxide aid in obtaining high temperatures.

In connection with the relation between coke hardness, specific gravity, and porosity, Mott and Wheeler (264) state:

> From a study of the general properties of cokes we have tested, it appears that the average temperature of the fuel bed is lower the lower the impact hardness, real specific gravity, and total porosity.

This indicates that high porosity is an aid in obtaining high temperatures, provided it can be obtained without sacrificing strength or resistance to size degradation. According to Mott and Wheeler:

> The porosity of coke appears to be of minor importance in blast-furnace practice. A high value seems to be desirable, but it is probably not worth while to attempt to increase the porosity directly.

The features of coke structure emphasized by these investigators are uniformity and paucity of enlarged pores and fractures. Although microstructure most likely influences hardness and combustibility, no correlation of these properties was obtained.

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Limestone

Silica in limestone decreases the amount of CaO and MgO available for fluxing the ore gangue and coke ash. The amount of limestone required and the slag volume increase sharply as the silica in the limestone increases. Although a poorer grade of limestone may be available at a lower price, it should not be used without the advice and consent of the furnace operator.

Operating Details of Ferromanganese Furnaces

The operation of furnaces producing ferromanganese is characterized by low blast pressure, regular settling of the stock, and loss of few tuyères. Little difficulty is experienced in controlling silicon. Sulphur presents no problem. Operating problems center upon ways and means of recovering in the metal the maximum percentage of manganese charged consistent with fuel consumption and output. Conditions that favor high recovery of manganese are: Small slag volume, a basic slag, high blast temperature, and coarse ores which do not break down excessively.

Percentage of Manganese in the Slag

The selection of raw materials is important in controlling slag losses. When the raw materials remain constant the loss of manganese in the slag is held to a minimum by varying the basicity of the slag, the rate of driving, and the hearth temperature. The optimum basicity of slag for maximum recovery of manganese will depend somewhat upon the amount of reduction of MnO above the tuyeres and upon the temperature to which the blast can be heated. Brassert (37) states that through the use of the highest blast temperature (1,470° F.) the slag can be kept fluid enough in spite of being very "limey", and the manganese in the slag can be held uniformly below 6 percent. Royster (322, p. 129) found in studying data on ferromanganese furnaces operated during the war that when the average slag basicity was increased from 1.19 to 1.77 the manganese in the slag decreased from 14.2 to 7.4 percent. Data on British furnaces by Clements (49, p. 350) include slag basicities of 1.63, 1.91, 1.98, and 1.71, with corresponding manganese in the slag of 11.09, 7.27, 8.16, and 8.47 percent. As previously pointed out, low slag loss is usually accompanied by high volatilization loss.

Function of Bases in Reduction of Manganese

The addition of bases to charges of ferromanganese furnaces serves two purposes. It is well-known that the fusibility of a slag depends upon the character of the bases as well as upon the proportion of bases and silica. The total heat of solidification, which includes the heat of solidification plus the heat evolved in cooling from the melting point down to room temperature, is an index of fusibility. Hofman (164) has shown the influence of replacement of MnO by CaO upon the total heats of solidification or the fusibility of slags containing varying amounts of silica. In general, the total heat of solidification increases as MnO is replaced by CaO, thus showing that the presence of bases in the charge retards the formation of fluid

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manganese silicates and hence aids in producing slag with higher free-running temperatures. Such slag reaches the crucible at a higher temperature which favors lower slag losses of manganese.

The slag in the crucible of a ferromanganese furnace is a solution of complex compounds. The activity of these compounds is affected by the amount of thermal dissociation. Moreover, manganese may exist as an infusible constituent. It appears that increased CaO makes the MnO more available for reduction. This may be accomplished by reaction with infusible compounds and the formation of slag constituents more susceptible to thermal dissociation.

Blast Temperature

About one half of the heat required to produce 1 ton of pig iron is introduced as sensible heat in the hot blast used to make 1 ton of ferromanganese. The quantity of heat thus introduced is not as important as the effect blast temperature has upon the prevailing temperature of the slag, metal, and tuyères. Richards (314) states that an increase of 100° C. in blast temperature raises the theoretical temperature before the tuyères 85° C. Royster, Joseph, and Kinney (326) found from observations on the tuyères of an experimental blast furnace that the temperature in front of the tuyères increased about 1° for every 2° rise in blast temperature. This observed change is about one half the theoretical calculated change. It is very difficult to isolate the effect of any one variable in blast-furnace practice. For this reason there is no established relation between blast temperature and temperature of the slag, metal, and tuyères. Reference has been made to the excellent practice reported by Brassert (37). With a blast temperature of 1,470° C., which is several hundred degrees higher than the average blast temperature, the coke per ton averaged 3,896 pounds for a month; the slag contained 5.81 percent manganese. A small amount of coal (288 pounds per ton) was used to reduce top temperatures and to minimize volatilization losses. With the use of a Cottrell treater much of the volatilization loss and dust loss may be recovered. The fact that the material so recovered is pyrophoric indicates that it is to a considerable extent metallic manganese.

Rate of Driving

Various methods have been used on rating the operating speed of blast furnaces, such as pounds of carbon per square foot of hearth area per minute, pounds of coke per cubic foot of working volume per 24 hours, and pounds of coke per square foot of bosh area per minute. Royster (322, p. 127) suggested the pounds of gross slag (MnO included in slag-forming materials) per square foot of hearth area per minute as a criterion for rate of driving. Gross slag includes the MnO equivalent of all of the manganese in the charge, which implies that all of the "metallic" manganese is produced in the hearth from the molten slag. This is a highly doubtful assumption. When this rule for speed of operation was applied to furnaces producing ferromanganese during the war, the manganese in the slag increased 1.34 percent for an increase of 1 pound of slag per minute per square foot of hearth area. The advantage of such a basis for governing the speed of operation is that it takes into account the size of the furnace as well as the grade of raw materials. Furnaces using more siliceous materials from which larger slag volumes would be produced would properly be blown at a slower rate.

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TABLE 74. - Data on British ferromanganese practice (by Elements)

	I	II	III	IV
Lines of furnace	Height of furnace ..... feet 71 Hearth diameter ..... do 9 Bosh diameter ..... do 18 Bosh height ..... do 15 Bosh angle ..... 73° 20' Distance from tuyeres to hearth bottom feet 6 Big bell clearance ..... do 2 Stock-line diameter ..... do 14½	..... 71 ..... 9 ..... 18 ..... 16 ..... 75° 20' ..... 6 ..... 2 ..... 14½	Height of furnace ..... feet 71 Hearth diameter ..... do 9 Bosh diameter ..... do 18 Bosh height ..... do 16 Bosh angle ..... 75° 20' Distance from tuyeres to hearth bottom feet 6 Big bell clearance ..... do 2 Stock-line diameter ..... do 14½	
Output (Per day ..... tons of metal. (Per working hr. do	73.2 3.1	85.4 3.6	88.65 3.8	83.06 3.5
Class of metal	80 percent ferromanganese	78 percent ferromanganese	78-79 percent ferromanganese	78 percent ferromanganese
Net blowing time per week ..... hours	164	164	161	164
Yields from burden (excluding coke) (Manganese ..... % (Iron ..... do (Mn/Fe ratio	33.53 3.76 8.92/1	35.72 3.88 9.21/1	36.56 4.025 9.08/1	34.61 4.53 7.64/1
Yields from total charge (including coke) (Manganese ..... % (Iron ..... do (Mn/Fe ratio	19.34 2.945 6.56/1	19.32 2.943 6.57/1	20.048 2.945 6.801/1	19.05 3.12 6.106/1
Coke per ton of metal .....lbs.	4,648	5,145	4, 842	5,136
Analysis of metal ..... percent	Mn 80.8 Fe 12.4 Si 0.61 P 0.253 C 6.94	Mn 78.05 Fe 14.15 Si 0.705 P 0.249 C 6.76	Mn 78.58 Fe 13.82 Si 0.572 P 0.241 C 6.7	Mn 78.11 Fe 14.09 Si 0.689 P 0.248 C 6.68
Area of hearth ..... sq. ft.	63.62	63.32	63.62	63.62
Area of bosh ..... do	254.47	254.47	254.47	254.47
Metal produced per hour per sq. ft. of hearth ..... lbs.	110	128	136	125
Metal produced per hour per sq. ft. of bosh ..... do	28	32	34	31
Burden per ton of metal ... do	Raw ore (1) 1,819 Raw ore (2) 1,835 Raw ore (3) 869 Limestone 1,598 Pyrites Res. 150	Raw ore (1) 3,286 Raw ore (2) 542 Raw ore (3) 544 Limestone 1,604 Flue dust 43 Pig bed scrap 43 Broken cast iron 2	Raw ore (1) 3,043 Raw ore (2) 27 Raw ore (3) 31 Raw ore (4) 1,130 Limestone 1,547 Flue dust 40.5 Pig bed scrap 40.5	Raw ore (1) 3,029 Raw ore (2) 458 Raw ore (3) 523 Raw ore (4) 542 Limestone 1,648
Classes and derivation of ores used	(1) Indian manganese ore (C.P.P.S.) (2) Georgian manganese ore (Caucasus) (3) Brazilian manganese ore (Lafayette)	(1) Indian manganese ore (C.P.P.S.) (2) Georgian manganese ore (Caucasus) (3) Brazilian manganese ore (Lafayette)	(1) Indian manganese ore (C.P.P.S.) (2) Georgian manganese ore (Caucasus) (3) Brazilian manganese ore (Lafayette) (4) Gold coast manganese ore	(1) Indian manganese ore (C.P.P.S.) (2) Georgian manganese ore (Caucasus) (3) Brazilian manganese ore (Lafayette) (4) Brazilian manganese ore (Wigge-Miguel-Burnier)
Analysis of ores ..... percent	(1) (2) (3) Mn 46.73 45.36 44.20 Fe 6.03 .99 2.30 SiO_2 8.32 9.65 8.19 P .10 .16 .05 Moist. 1.00 8.58 7.06	(1) (2) (3) Mn 50.90 45.67 42.64 Fe 6.09 .84 3.86 SiO_2 7.69 9.35 3.86 P .96 .186 .08 Moist. 1.37 8.28 8.82	(1) (2) (3) (4) Mn 50.89 45.83 42.9 48.88 Fe 5.75 .86 4.0 3.97 SiO_2 7.31 9.51 3.95 2.25 P .091 .188 .082 .105 Moist. .48 8.0 8.76 4.2	(1) (2) (3) (4) Mn 49.96 45.76 42.88 38.65 Fe 6.20 .88 3.80 5.48 SiO_2 8.50 9.30 3.95 1.84 P .104 .178 .086 .032 Moist. 1.20 7.60 8.90 20.00
Proportion of rough, rubble, and fines ..... percent	(1) (2) (3) Rough 70) 60 Rubble 20) 10 10 Fines 10 90 30	(1) (2) (3) Rough 70) 65 Rubble 20) 10 20 Fines 10 90 15	(1) (2) (3) (4) Rough 70) 65 60 Rubble 20) 10 20 30 Fines 10 90 15 10	(1) (2) (3) (4) Rough 70) 60) Rubble 20) 10 10) 20 Fines 10 90 30 80
Classes and derivation of fluxes used	Limestone, as quarried.	Limestone, as quarried.	Limestone, as quarried.	Limestone, as quarried.
Analysis of flux ..... percent	MnO Fe_2O_3 SiO_2 Al_2O_3 CaO MgO CO_2 0.4 0.6 1.5 0.1 53.0 0.6 42.67	MnO Fe_2O_3 SiO_2 Al_2O_3 CaO MgO CO_2 0.3 0.6 1.8 0.56 53.8 0.4 42.5	MnO Fe_2O_3 SiO_2 Al_2O_3 CaO MgO CO_2 0.24 0.68 2.6 1.1 53.14 0.32 42.0	MnO Fe_2O_3 SiO_2 Al_2O_3 CaO MgO CO_2 0.26 0.76 2.20 0.70 53.0 0.68 42.0
Physical condition of fluxes	Rough, 90 percent; rubble, 5 percent; fines, 5 percent.	Nearly all lumps.	Nearly all lumps of about ¾- to 4-in. cubes.	Crushed and screened - Rough, 90 percent; rubble, 5 percent; fines, 5 percent.
Classes and derivation of other materials used	Pyrites residues from S. kilns of Chemical Works	(1) Broken cast iron (2) Heavy flue dust from dry dust catcher (3) Riddlings from pig beds	(1) Heavy flue dust from dry dust catcher (2) Riddlings from pig beds	(1) Heavy flue dust from dry dust catcher (2) Riddlings from pig beds
Analysis of other materials ..... percent	Fe_2O_3 SiO_2 Al_2O_3 $Na_2O + K_2O$ S H_2O (free) 75.0 4.22 0.97 0.25 0.72 18.5	Fe Mn C P S CaO SiO_2 Al_2O_3 (1) 95.0 0.8 3.8 0.8 0.05 - - - - - - (2) 3.4 20.1 8.7 - - - - 12.1 12.9 6.1 (3) 5.7 16.7 - - - - - - 61.3 - -	Fe Mn CaO SiO_2 Al_2O_3 C (1) 2.6 16.7 13.2 11.0 5.3 11.5 (2) 8.3 19.5 - - 56.3 - - - -	Fe Mn CaO SiO_2 Al_2O_3 C (1) 3.0 18.4 11.0 13.6 6.0 8.0 (2) 7.6 18.8 - - 56.2 - - - -
Physical condition of other material	Nearly all fines.	(1) All lumps. (2) All fines. (3) All rubble.	(1) All fines. (2) All rubble and small lumps.	(1) All fines. (2) All small lumps and rubble.

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TABLE 74. - Data on British Ferromanganese Practice (by Elements)--Continued

Lines of furnace	I	II	III	IV
Height of furnace	feet 71	71	feet 71	feet 71
Hearth diameter	do 9	9	do 9	do 9
Bosh diameter	do 18	18	do 18	do 18
Bosh height	do 15	16	do 16	do 16
Bosh angle	73° 20'	75° 20'	75° 20'	75° 20'
Distance from tuyères to hearth bottom	feet 6	6	feet 6	feet 6
Big bell clearance	do 2	2	do 2	do 2
Stock-line diameter	do 14½	14½	do 14½	do 14½
Observed time materials are in furnace ..... hours	Approx. 18	Approx. 15	Approx. 15	Approx. 15
Weight of slag per ton of metal made ..... lbs.	2,148	2,475	1,848	2,495
Analysis of slag ..... %	SiO_2 26.1; CaO 41.3; MgO 1.2; Al_2O_3 12.0; MnO 14.33; (Mn) 11.09	SiO_2 24.5; CaO 45.85; MgO 1.1; Al_2O_3 13.13; MnO 9.38; (Mn) 7.27	SiO_2 23.8; CaO 45.0; MgO 0.85; Al_2O_3 14.2; MnO 10.53; (Mn) 8.16	SiO_2 25.6; CaO 43.1; MgO 0.8; Al_2O_3 13.9; MnO 10.93; (Mn) 8.47
	FeO 0.45; BaO 2.2; Na_2O 0.19; S 2.68	FeO 0.26; BaO 2.10; Na_2O +K_2O 0.47; S 2.34; SO_3 1.10	BaO 2.4; Na_2O +K_2O 0.38; S 2.08; SO_3 1.24	FeO 0.3; BaO 1.8; Na_2O +K_2O 0.36; S 2.4; SO_3 0.9
Analysis of (By vol. ... %	CO_2 5.77; CO 31.98; H_2 2.11; CH_4 1.09; N_2 59.02	CO_2 6.1; CO 31.6; H_2 2.83; CH_4 0.67; N_2 58.8	CO_2 5.6; CO 31.7; H_2 2.8; CH_4 0.7; N_2 59.2	CO_2 6.3; CO 31.2; H_2 2.0; CH_4 0.7; N_2 59.8
exit gases (By wt. .... do	9.0; 31.7; 0.15; 0.62; 58.5	9.6; 31.4; .2; .38; 58.42	8.8; 31.6; .2; .4; 59.0	9.76; 30.76; 0.14; 0.39; 58.95
Temperature of exit gases	940° F. 507° C.	895° F. 479° C.	915° F. 491° C.	885° F. 474° C.
Density of gas per cu. ft. at 32°F. & atmos..... lbs.	0.0791	0.0788	0.0786	0.795
Vol. of gas per pound at 32°F. & atmos. .. cu. ft.	12.65	12.68	12.72	12.57
Analysis of coke ..... %	F.C. 79.66; Ash 6.20; Moist. 1.44; V.M. 1.51; S 0.05; P_2O_5	F.C. 79.0; Ash 13.94; Moist. 5.8; V.M. 1.26; S 1.82; P_2O_5 0.05	F.C. 80.7; Ash 10.0; Moist. 8.0; V.M. 1.3; S 1.56; P_2O_5 0.08	F.C. 80.4; Ash 13.2; Moist. 4.8; V.M. 1.6; S 1.56; P 0.04
	MnO 0.20; Fe_2O_3 2.63; SiO_2 4.0; Al_2O_3 2.5; CaO 0.77; MgO 0.31; K_2O+Na_2O 0.30	MnO 0.20; Fe_2O_3 2.60; SiO_2 4.94; Al_2O_3 3.0; CaO 0.54; MgO 0.26; K_2O+Na_2O 0.30	MnO 0.10; Fe_2O_3 2.34; SiO_2 3.0; Al_2O_3 2.2; CaO 0.36; MgO 0.10; K_2O+Na_2O 0.22	MnO Tr.; Fe_2O_3 2.0; SiO_2 4.7; Al_2O_3 2.8; CaO 0.4; MgO 0.18
Character of coke	Hard and dense	Hard and dense	Hard and dense	Hard and dense
Physical condition of coke	Lumps up to 12-in cubes: very little breeze	Lumps up to 12-inch cubes: very little breeze	Lumps up to 12-inch cubes: very little breeze	Lumps up to 12-inch cubes: very little breeze
Carbon charged per ton of metal ..... lbs.	3,703	4,064	3,908	4,130
Carbon charged per hour per sq. ft. of bosh ... do	45	58	59	58
Carbon charged per hour per sq. ft. of hearth . do	182	233	237	230
Pressure of blast per sq. in. ..... lbs.	6	6	6.05	5.8
Temperature of blast	1,152° F. 622° C.	1,173° F. 634° C.	1,184° F. 640° C.	1,180° F. 638° C.
Calc. wt. of blast/min..lbs.	906.15	1,152	1,189	1,166
Calc. vol. of blast/min. at 32° F. & atmos. .. cu.ft.	11,229	14,275	14,733	14,448
Calc. vol. of blast/min. at actual temp. & press..do	26,110	32,890	34,850	34,460
No. and diameter of tuyères	Eight - 5-3/4 inches	Eight - 5-3/4 inches	Eight - 5-3/4 inches	Eight - 5-3/4 inches
Velocity through tuyères ..... ft. per sec.	302	375	398	393
Calc. wt. of exit gases per min. at 32° F. & atmos. ..... lbs.	1,192.1	1,519	1,552	1,523
Calc. vol. of exit gases /min. at 32° F. & atmos. ..... cu.ft.	14,772	18,822	19,231	18,872
Wt. of dust recovered per ton of metal made ..... lbs.	275.5	320 (est.)	350 (est.)	320 (est.)
Analysis of dust ..... %	Fe_2O_3 4.0; MnO 21.3; (Mn) 16.5; Al_2O_3 6.35; CaO 13.62; MgO 0.5	Fe_2O_3 5.9; MnO 25.2; (Mn) 19.52; Al_2O_3 5.0; CaO 14.34; MgO 0.56	Fe_2O_3 5.6; MnO 22.1; (Mn) 17.12; Al_2O_3 5.1; CaO 15.32; MgO 0.44	Not given
	K_2O 14.85; Na_2O 3.62; SiO_2 12.9; CO_2 10.16; SO_3 8.92; Cl_2 3.95	K_2O 13.92; Na_2O 3.34; SiO_2 11.46; CO_2 9.2; SO_3 7.26; Cl_2 3.42	K_2O 13.26; Na_2O 3.1; SiO_2 11.8; CO_2 11.3; SO_3 8.63; Cl_2 3.24	do
Sum- (Manganese to metal..%	84.73	80.31	82.17	80.41
-ma- (Manganese to slag ..do	11.04	8.27	7.04	9.71
-y (Manganese to stack..do	(4.23 (by difference) (2.14 (by experiment)	11.42 (by difference)	10.79	9.88 (by difference)

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Clements has compared the output of furnaces in terms of pounds of metal per square foot of hearth area per hour and per square foot of bosh area per hour (table 74) (49, table 37). On the basis of hearth area, the output of a group of American ferromanganese furnaces operated during the war ranged from 44 to 60 pounds compared with 110 to 136 pounds for four British furnaces. The metal produced per square foot of bosh area per hour ranged from 21 to 30 pounds in the American furnaces and from 28 to 34 pounds in the British furnaces. The slower rate of production in the American furnaces was due principally to the extensive use of domestic siliceous ores, whereas high-grade Indian, Caucasian, and Brazilian ores were used in the British furnaces. In general, a furnace capable of producing 500 tons of pig iron per day will have an output of 90 to 125 tons of ferromanganese. Recoveries can be increased by slower driving up to the point at which increased costs above raw materials make further recovery uneconomical.

Stack Loss

The amount of manganese carried out with the top gases either as ore dust or fine fumes, due to volatilization of manganese, usually is determined by difference; the manganese recovered in the slag and metal is deducted from the manganese charged. Values obtained in this way are subject to errors in calculating the weight of slag as well as to errors in the weights and analyses of raw materials and products. Exact determination of the amount of dust carried off in large volumes of gases is difficult, therefore dust losses are not susceptible to accurate measurement directly. The brown fumes issuing from the stove of ferromanganese furnaces and the necessity of frequently cleaning the stoves are evidence that substantial amounts of manganese are carried off with the gases in a finely divided condition. There is apparently no published information as to how much of the total stack loss consists of granular ore particles and how much consists of fine powder or fumes. Langhorne (220) states that minus 20-mesh particles do not seem to stay in the furnace, thus increasing the loss of manganese. He also points out that the physical character of the ore as charged does not always give an index of dusting characteristics because soft ores, which may be fairly coarse, are susceptible to size degradation in the furnace through contact with coke. The ratio of coke to ore by volume is much greater than in pig-iron furnaces and, hence, the opportunity for ore particles to be caught and crushed between lumps of coke is much greater. Joseph and Barrett (186) found that five imported manganese ores were little affected by cold mechanical work, but the average particle size was decreased 40 to 50 percent as a result of a moderate amount of mechanical work at 1,400° F. Nearly 50 percent of one ore was finer than 14-mesh after a decrepitation test. These tests indicate that manganese ores may break down a great deal when heated and subjected to the abrasive action of coke in a ferromanganese blast furnace. It seems likely that a substantial portion of the so-called stack loss is an ordinary dust loss, which varies depending upon the amount of fine material in the ore burden and upon the extent to which the ore mixture breaks down in the furnace.

The volatilization of manganese should increase as the hearth temperature increases. Royster found no systematic variation of stack loss with increased hearth temperature, as indicated by the high-silicon metal, excess carbon, basic slag, and low manganese in the slag. This apparent lack of relationship

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is not surprising, considering the chances for error in arriving at stack losses by difference. It is known from practice that dust losses vary widely with the character of the ore and the distribution of stock which governs channeling of the gases. The ores used in the furnaces investigated by Royster came from many sources and varied widely in character. Losses due to dusting of the ore might very easily mask variations in volatilization losses. Although the exact amount of manganese carried off with the gases is a quantity not susceptible to accuracte measurement, it is an important item in furnace practice, ranging from 5 to 20 percent of the manganese charged.

Composition of Dust from Ferromanganese Furnaces

The composition of the dust recovered from ferromanganese furnaces raises some interesting questions. An examination of the analyses of raw materials and of the dust samples given in table 74 shows that the dust contains more iron in proportion to manganese than the charge. Why should iron, a less-volatile metal occurring in much smaller amounts in the charge, be concentrated in the dust? The ratio of manganese to iron in the charge of three British furnaces ranged from 8.92 to 9.21, exclusive of coke, and from 6.6 to 6.8, inclusive of coke. The reported composition of dust samples taken from these same furnaces shows a manganese-iron ratio of 4.1:5.9. One would naturally expect to find a concentration of manganese in the dust rather than a concentration of iron. Royster found that 6.5 percent of the iron charged into a furnace did not appear in the slag and metal. It appears that substantial amounts of coke ash, formed on the surface of the coke as a fine powder, are carried by the gases up through the porous and comparatively hot column of stock and out of the furnace. It is generally considered that the ferro-grade ores should contain about nine times as much manganese as iron. If the iron in the coke is taken into consideration, the average charge contains 6 to 7 times as much manganese as iron. The evidence points very strongly to a loss of at least a portion of the iron in the coke in the manner indicated.

Exclusive of the coke, the charge of two British furnaces operating on high-grade ores contained about five times as much manganese as silica (table 74). Dust samples from these same furnaces contained 1.5 to 1.7 times as much manganese as silica. There is a concentration of silica in the dust which cannot be explained as a dust loss from the charge, unless an air classification of silica is assumed to occur. This concentration of silica in the dust is more likely due to coke ash carried off in the exit gases. Alumina is also concentrated in the dust in a similar way.

Limestone is not readily abraded by coke before calcination, but after calcination is susceptible to abrasion. The presence of some 12 to 15 percent calcium oxide, compared to 20 to 25 percent MnO in the flue dust from furnaces producing ferromanganese, is due to abrasion followed by dusting.

The relative amount of Fe_2O_3, SiO_2, CaO, Al_2O_3, and MnO in the dust samples, reported by Clements, suggests that the loss of manganese by volatilization has been given undue emphasis in the literature dealing with the production of ferromanganese in the blast furnace. Resistance of manganese ores to size degradation in the furnace and the size of the ore as charged have an important bearing on the amount of dust produced and suggest more careful size preparation of the ores as a means of decreasing the so-called "stack losses."

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It appears that much of the so-called volatilization loss in the form of fine fumes may be due to oxidation before the tuyeres, followed by dusting.

Furnace Lines

Furnaces producing ferromanganese operate smoothly without hanging or slipping, a natural result of a porous change which offers little resistance to gas flow and results in low pressures. The slow rate at which air is supplied also tends to produce low pressures, which promote regular settling of the charge. As a result of this freedom from mechanical troubles, the shape of furnaces producing ferromanganese has not received the same consideration as the shape or lines of pig-iron furnaces. It is common practice in plants which produce pig iron and ferro-alloys to put furnaces on ferromanganese or spiegel after the lining has been worn to such an extent that smooth operation on pig iron is impossible. Smaller furnaces, in general, are used in producing ferro-alloys.

Location of Plants Producing Ferromanganese

Smith (352) reports that ferromanganese was produced at the following domestic plants in 1929:

Bethlehem Steel Co., Johnstown, Pa.
Colorado Fuel & Iron Co., Pueblo, Colo.
Lavino Furnace Co., Reusens, Va.
Ohio Ferro-Alloys Corporation, Philo, Ohio.
Pittsburgh Metallurgical Co., Niagara Falls, N. Y.
Tennessee Coal, Iron & Railroad Co., Bessemer, Ala.
United States Steel Corporation, Etna and Pittsburgh, Pa.

Electric furnaces were used by the Ohio and New York companies. In 1928, ferromanganese was produced at seven furnaces by three companies.

Production of Ferromanganese in Electric Furnace

Ferromanganese can be produced in the electric furnace from a proper charge of ore, coal or coke, and limestone. If arcing from the electrodes to the bath is avoided volatilization losses are not excessive. As in other electric-furnace operations, cheap power is necessary for economical operation. The important features of the operation are: Power and electrode requirements, size and type of furnace, amount and type of reducing agent, and character of slag losses.

Keeney (196) states that the power per ton of ferromanganese ranges from 4,000 kw.-h. in a 3,000-kw. furnace to 7,000 kw.-h. in a 1,000-kw. furnace. The electrode consumption is 150 to 250 pounds of amorphous carbon electrodes per ton. Power and electrode requirements will vary with the grade of raw materials used. Gillett and Williams (112) used 431 pounds of graphite electrodes per ton per 1,000 kw. of power in calculating the cost to produce ferromanganese from siliceous domestic ores.

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Keeney and Lonergan (197) have described a 1,200-kva furnace and an 1,800-kva furnace in producing ferromanganese. The description includes details of the two rectangular, three-electrode furnaces, transformers, electrode holders, and secondary bus systems. Reducing agents, calculations of the charge, and method of operation are discussed. Difficulties of operation which may be encountered include formation of carbides, "blowing" failure of bottom, tapping, failure of electrode holders, and bridging of the charge.

Voltages (electrodes to the charge) range from 55 to 100, depending upon the size of the furnace. Charging may be continuous or intermittent. Coke, coal, lignite, and charcoal may be used as reducing agents. The quantity required varies, depending upon the grade of raw materials. Magnesite or carbon may be used to make the furnace bottom. Metal and slag are usually tapped at 2-hour intervals.

Keeney (196) reports an average slag containing 35.4 percent CaO, 5.81 percent MgO, and 37.79 percent SiO_2, or a ratio of $\frac{CaO + MgO}{SiO_2}$ of 1.43:1. Slags somewhat more basic than this are preferred in the blast furnace. A basic slag will lead to more complete elimination of manganese from the slag, provided ample time is allowed. If the rate of charging is too rapid additional bases may lower the recovery, because a slight decrease of manganese in the slag would be offset by the increase in the weight of the slag. With a proper adjustment, however, of tonnage for a given furnace, basic slags aid in controlling silicon in the alloy and decrease the loss of manganese in the slag.

Manganese ores break down to dust even in the electric furnace. It is not possible therefore to differentiate between dust losses and losses by volatilization. The combined loss from dusting and volatilization is 5 to 10 percent. Slag loss depends to a large extent upon the silica in the ore, which, in turn, governs the weight of slag per ton of alloy. The total losses will be 10 to 30 percent depending upon the grade of ore used. With high-grade ores a 90 percent recovery of manganese can be realized. When smelting siliceous ores the loss due to volatilization and dusting will amount to one-fourth to one-sixth of the total conversion loss, whereas with the best grades of ore the loss of slag may about equal the combined loss by dusting and volatilization.

Production of Low-Carbon Ferromanganese

Standard ferromanganese, containing about 7 percent carbon, cannot be used in producing extremely low-carbon steel. Either medium- or low-carbon ferromanganese is used in making additions to such steel. Very little recent information has been published upon the production of low-carbon ferromanganese.

Roberts and Wraight (316, pp. 250-282) investigated various methods for decarburizing ferromanganese, which may be grouped as follows:

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1. Replacement of combined carbon by silicon.
2. Replacement of combined carbon by aluminum.
3. Cementation in various metallic oxides.
4. Fusion at high temperatures with lime.
5. Bessemerization of the alloy with air, CO_2, and H_2.
6. Oxidation of carbide by manganous oxide.

The most satisfactory results were obtained by the sixth method, that is, fusion with manganous oxide.

As pointed out by Coutagne (60), Moissan showed by obtaining alloys with 3 to 4 percent carbon by reduction of MnO with carbon in the presence of excess MnO that the reaction

$$Mn_3C + MnO = 4Mn + CO$$

will proceed at the high temperature attainable in the electric furnace. He also states that if manganese carbide is formed first, which might be the case, it is subsequently partly refined, or, if manganese is formed, first, carbon absorption will depend upon the amount of oxide present. Whatever the mechanism of reduction may be, this is an expensive method for producing manganese with low carbon content.

The refining action of manganous oxide upon manganese carbide is the basic feature of patents by Humbert (173) and Hadfield (134). Humbert's patent proposes to decarburize commercial ferromanganese by electrically heating it to temperatures above 1,700° C. in the presence of manganous oxide. Small coke or ferrosilicon is used to reduce part of the manganous oxide. According to Hadfield's procedure, commercial ferromanganese is treated with manganese ore and enough carbon to reduce the higher oxides in the ore to manganous oxide. After gradually building up a bath of ferromanganese and slag rich in MnO and therefore viscous, ferrosilicon is added to reduce part of the manganous oxide. The silica formed by reduction of MnO with silicon increases the fluidity of the slag. Lime additions are made to control the fluidity of the slag. Calcium silicide may be added shortly after the final addition of ferrosilicon. The materials used in a heat, cited to illustrate the process, were as follows: 15 cwt. of ferromanganese, 5-1/2 cwt. of manganese ore, 44 pounds of 50 percent ferrosilicon, and 17 pounds of calcium silicide. The alloy produced contained 71.6 percent manganese and 1.54 percent carbon.

Coutagne (60) states that the most likely process and the one most widely used consists in refining silicomanganese by treatment with manganese ore. The silicomanganese is first produced in the electric furnace. A charge of such an alloy is next treated with manganese ore, the materials involved in heat cited being as follows:

	Lb.
Silicomanganese (2.7 percent C, 60 percent Mn, and 13 percent Si)	1,320
Turnings	110
Mineral (35 percent Mn)	880
Lime	880

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The metal produced from such a charge weighed 1,540 pounds and analyzed as follows: 2.5 percent carbon, 53 percent manganese, and 1.77 percent silicon. If an alloy containing 75 percent manganese, 20 to 25 percent silicon, and 1.0 percent carbon is used, this mode of operation is reported to yield alloys containing less than 1.0 percent carbon.

Becket (19) has recently patented a similar process for producing low-carbon ferromanganese. In two examples which he cited, the following materials were used:

	No. 1	No. 2		No. 1	No. 2
Weight of alloy .. lb.	14,948	16,443	Weight of alloy ... lb.	26,935	26,389

Analysis of charge, percent:

Alloy:			Ore:
Mn	64.44	68.30	56.50 (largely as MnO_2)
Si	24.66	23.13	2.17 Fe
C	.84	.67	

Balance largely iron.

Analysis of metal produced, percent:

Mn	80.11	83.91
Si	1.22	1.83
C	1.25	1.08

Balance largely iron.

The manganese-silicon alloy and the manganese ore were ground to pass 100 mesh and thoroughly mixed and dried. The silicothermic reduction of the manganous oxides was self-propagating after the charge was locally heated to a temperature sufficient to initiate the reaction. No apparatus is required except a refractory pot or vessel to hold the charge. The carbon content of the manganese alloy is controlled by selecting a manganese-silicon alloy of appropriate composition. For example, Beckett states that a manganese-silicon alloy containing 1.0 percent carbon and 20 percent silicon may be used in producing an alloy with about 1.5 percent carbon, while a manganese-silicon alloy containing 0.7 percent carbon and 24 percent silicon yields a product containing about 1.0 percent carbon. A product still lower in carbon is produced by using a manganese-silicon alloy containing more silicon and less carbon.

The slag produced in the heats cited by Beckett contained about 65 percent MnO. It can be smelted in an electric furnace to produce manganese-silicon alloys similar in composition those described. Slag from this operation contains about 15 percent MnO and is discarded.

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The production of low-carbon manganese alloys on a commercial scale is a comparatively new development. Few data have been published regarding the practical details of the operation.

PRODUCTION OF SPIEGELEISEN

The factors that characterize good practice in producing ferromanganese, the 80 percent alloy, apply in a modified degree to the production of spiegeleisen, the 20 percent alloy. Low-silica charges, slow blowing, and regulation of the slag basicity to minimize slag losses are important in the production of both alloys. The fuel requirements, tonnage, and recovery depend upon the amount of silica in the charge. Royster (322, p. 117) reported an average fuel consumption of 3,950 pounds of coke per ton of 16 to 20 percent alloy for furnaces operating during the World War. The slag averaged 9.68 percent manganese. This fuel consumption and the percentage of manganese in the slag are much higher than was obtained in furnace practice summarized by Brassert (37), who reported an average figure of 2,858 pounds of coke per ton of 19 percent alloy and 2.18 percent manganese in the slag. High prices during the war stimulated efforts to produce tonnage often at the sacrifice of manganese recovery. This condition, together with the siliceous charge used at that time, accounts for the poorer practice reported by Royster. According to Brassert, a furnace having a normal daily capacity of about 500 tons of pig iron will produce about 375 tons of spiegel per day. This, however, implies the use of good raw materials and stoves which will produce high blast temperatures.

Production of High-Silicon Spiegel

The work of Herty and Fitterer on the deoxidation of steel with manganese-silicon alloys has created interest in high-silicon spiegel. They have reported (152) that a ratio of manganese to silicon of 4.5:6.0 gave the best results in deoxidizing both basic open-hearth and acid open-hearth heats ranging from 0.12 to 0.6 percent carbon. Such a ratio of manganese to silicon would require about 4 percent silicon in normal spiegel containing 20 percent manganese.

Restrictions as to grade of manganese alloys were modified during the World War to permit wider use of lean and siliceous domestic ores. The standard for spiegel was lowered from 20 to 16 percent manganese. The production of occasional lots of high-silicon spiegel of this grade was a natural consequence of a furnace practice evolved rather quickly for treating siliceous ores. Operating data on the production of such lots of spiegel are given in table 75. The ratios of manganese to silicon are 4.8, 3.4, 5.5, and 3.7 for test periods 41, 42, 68, and 70, respectively. No mention is made of any peculiarities or operating difficulties encountered in these test periods. One may assume, therefore, that the operation was similar to normal spiegel practice. The manganese content of the metal could have been raised to 20 percent by use of an ore mixture containing a higher ratio of manganese to iron. A higher fuel consumption and lower rate of driving would have increased the poor recovery of manganese in furnace C.

An examination of the data in table 75 indicates that temperature and rate of driving have foremost importance in producing high-silicon spiegel. The two

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test periods on furnace C show the importance of temperature. About 500 pounds of additional carbon and somewhat higher blast temperature increased the silicon in the metal from 3.1 percent for test period 41 to 4.9 percent for test period 42. This increase of 1.8 percent silicon in the alloy produced from the same raw materials in the same furnace illustrates the importance of temperature in the reduction of SiO_2. The decrease in output from 44.7 tons per day in period 41 to 30.2 tons in period 42 indicates that the production of high-silicon spiegel for a given furnace and set of raw materials will be less than that of standard spiegel. Further evidence of the decrease in tonnage as the silicon in the alloy increases appears in test periods 68 and 70 of furnace R, which produced 71.4 tons per day of spiegel containing 2.9 percent silicon and 59.3 tons of spiegel containing 4.4 percent silicon.

TABLE 75. - Operating Data from Blast Furnaces Producing High-Silicon Spiegel (by Royster) 1/

Period no. / Furnace			41 C	42 C	68 R	70 R
1.	Ore	pounds per ton	5,192	5,795	5,495	5,355
2.	Coke	do	3,327	3,831	3,853	5,048
2a.	Coal	do	749	926	-----	-----
3.	Limestone	do	1,568	2,052	3,728	3,480
	Ore analysis:					
4.	Mn	percent	12.72	12.77	10.35	9.06
5.	Fe	do	36.72	36.30	32.35	31.25
6.	SiO_2	do	17.46	16.65	19.97	16.48
7.	Spiegeleisen	tons per day	44.7	30.2	71.4	59.3
8.	Slag	pounds per day	2,614	2,990	4,585	4,735
9.	Mn in alloy	percent	14.9	16.5	15.9	16.1
10.	Si in alloy	do	3.1	4.9	2.9	4.4
11.	Blast temperature	°F.	1,234	1,304	768	909
12.	Top temperature	do	613	749	535	483
13.	Air per minute	cubic feet	8,660	8,740	28,800	21,300
	Slag analysis:					
14.	CaO	percent	26.0	24.3)	44.0	46.1
15.	MgO	do	10.1	11.1)		
16.	Al_2O_3		10.3	13.3	9.7	11.3
17.	SiO_2	do	38.3	37.2	36.3	36.3
18.	Mn	do	10.79	10.07	6.38	3.66
19.	Carbon	pounds	3,292	3,740	4,790	4,110
20.	Mn charged	do	660	740	563	486
21.	Mn to alloy	percent	49.0	50.6	63.4	73.6
22.	Mn to slag	do	42.6	40.7	51.8	35.6
23.	Mn lost in stack	do	8.4	8.7	-15.2	- 9.2

1/ Royster, P. H., Production of Manganese Alloys in the Blast Furnace: Chap. 8, Bull. 173 (Manganese--Uses, Preparation, Mining Costs, and the Production of Ferro-Alloys), Bureau of Mines, 1920, table 18, pp. 116-117.

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The recovery of manganese in furnace R was much higher than in furnace C, --63.4 and 73.6 percent compared to 49.0 and 50.6 percent. This is attributed to the use of more fuel per ton of metal in furnace R.

Basicity of Slag in Producing High-Silicon Spiegel

Slag basicity is important in controlling the silicon in all metal produced in the blast furnace, whether it be pig iron or alloys of manganese. The reduction of silica is not, however, controlled entirely by the character of the slag but by proper adjustment of temperature and rate of blowing, as well as slag basicity. For example, the ratios of bases to acids, $\frac{CaO + MgO}{SiO_2}$, was about 1.2 for test periods 41 and 42. Due, however, to an increase in the fuel, the silicon in the metal was 1.8 percent higher in period 42. (see table 75).

The slag basicity averaged 1.26, and the percent of silicon in the metal averaged 1.77 for a group of furnaces producing 16 to 20 percent spiegel during the World War. Two of these furnaces produced metal averaging 3.8 percent silicon, with an average slag basicity of 1.22.

From the meager operating data available it appears that spiegel containing 20 percent manganese and 4 percent silicon can be produced in the blast furnace from domestic ores without any unusual operating difficulties. Since manganese aids carburization and silicon retards it, one might expect that unusual amounts of "kish" or precipitated carbon would be formed in producing high-silicon spiegel. This assumes that carburization precedes the reduction of silica. The introduction of 4 percent silicon into metal containing 15 to 20 percent manganese and 5 to 6 percent carbon would decrease the carbon to about 3 percent.

Carbon precipitated as a result of increased silicon content or of a drop in temperature as the metal moves from the combustion zones to the crucible could be consumed by unreduced oxides in the slag or by oxygen from the blast.

During the blow-in period of the experimental blast furnace for investigating the smelting characteristics of high-manganese slag (see p. 230), several casts of high-silicon spiegel were produced over a 10-hour period. The average percentage composition of the metal and slag follows:

Metal, percent			Slag, percent				
Mn	Si	C	Mn	SiO_2	Al_2O_3	CaO	MgO
20.2	3.7	3.2	9.7	3.0	23.0	31.2	3.9

The ratio of bases to acids, $\frac{CaO + MgO}{SiO_2}$, for the average slag is 1.17 or very close to the basicity of the slag reported in table 73. No unusual features of operation were observed during the production of high-silicon spiegel in the experimental blast furnace.

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As pointed out by Coutagne (60, p. 212), the production of silicon-spiegel (10 to 12 percent Si and 18 to 20 percent Mn) in the blast furnace presents difficulties because the recovery of manganese requires a basic slag, while the reduction of silica is favored by an acid slag. This condition requires extra heat, which increases the cost of upkeep on the furnace lining and the loss of manganese by volatilization. As the ratio of silicon to manganese increases the observations noted above can be applied more rigorously. They apply to some extent to the production of spiegel containing 20 percent manganese and 4 percent silicon but are not important enough to throw the manufacture of this alloy from the category of the blast furnace into the category of the electric furnace.

Coutagne (60, p. 390) states that silicospiegel (10 to 12 percent Si) was made in the blast furnace by Pourcell in 1875 but the electric furnace offers advantages in cost and ease of producing a wide variety of alloys. Power requirements range from 2,500 to 3,000 kw.-h. when smelting a charge of high-grade manganese ore, turnings, quartz, and coke. The recovery of manganese from such a charge will range from 80 to 85 percent. If the charge consists of siliceous ore, turnings, limestone, coke, and spar the recovery is about 10 percent less.

Use of Ferruginous Manganese Ores in Production of Spiegel

The black ores of the Cuyuna range in Minnesota contain about three times as much iron as manganese, the approximate ratio necessary in producing 20 percent spiegel. These ores were used extensively during the World War but have not been mined extensively since that time because of their high silica content and comparatively high mining costs. The removal of silica from these ores will provide a supply of concentrate from which spiegel and high-silicon spiegel can be produced. The relative cost of units of manganese in the form of ferromanganese and in the form of spiegel required for the deoxidation of steel has no doubt been a factor in the transportation of spiegel over long distances. It appears therefore that the production of spiegel in middle western steel plants would stimulate wider use of this alloy.

A mill for concentrating the black ores of the Cuyuna range district was operated in 1931. The flow sheet is the result of work (67) at the Mississippi Valley Experiment Station of the United States Bureau of Mines in cooperation with a Minnesota mining company. Ore crushed to 5 mesh is classified and then tabled; the slimes from the tables are treated by flotation for additional recovery of fine iron and manganese. The daily capacity is about 500 tons of concentrate containing approximately 39 percent iron, 18 percent manganese, and 10 percent silica. Such a concentrate is well suited for the production of 20 percent spiegel. The ratio of manganese to iron would permit the production of a somewhat richer spiegel if this were desired.

Concentrates from the black Cuyuna ores could also be used in producing high-silicon spiegel (4 to 5 percent silicon). Concentrates would be superior to the crude ore for this purpose. Temperature is very important in producing high-silicon alloys. The required temperature can be obtained with less fuel when there is less silica in proportion to the iron and manganese in the charge. Lower silica would also permit higher recoveries and larger tonnages.

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Reduction of silica is a function of the ratio of silica in the charge to the bases and is not determined by the total amount of silica present.

There are deposits of ferruginous manganese ores in other parts of the country which could be used in producing spiegel. Transportation charges to steel centers would be prohibitive in many cases.

PRODUCTION OF HIGH-MANGANESE BASIC PIG IRON

Manganiferous iron ore shipped from the Lake Superior district in 1929 contained 157,590 tons of metallic manganese, about 43 percent of the total tonnage of manganese used that year in the form of ferro and spiegel. The metallic manganese derived from manganiferous iron ores increased more than tenfold from 1911 to 1929. Manganiferous iron ores are mixed with iron ores for the production of high-manganese basic pig iron (1.5 to 2.25 percent manganese). A tenfold increase in the quantity of manganese contained in the pig iron used in producing basic open-hearth steel did not decrease the amount of manganese added in the form of ferromanganese and spiegel. For example, in 1911 shipments of manganiferous iron ores from the Lake Superior district (largely from the Cuyuna range, Minnesota) contained 14,629 tons of metallic manganese. An average of 14.1 pounds of manganese was added as ferromanganese and spiegel to produce 1 ton of steel that year. Although shipments of manganiferous iron ore in 1929 contained 157,590 tons of metallic manganese, 14 pounds of manganese were used in the form of spiegel and ferromanganese to produce 1 ton of steel. It appears that increases in manganese specifications in steel have been sufficient to offset the small amount of residual manganese derived from basic pig iron.

Weld and others (385) concluded that the increased use of high-manganese pig iron probably would replace 15 percent of the manganese needed as ferromanganese and spiegel. At the time of their survey of the domestic manganese situation the trend in manganese consumption appeared to be downward. In view of this trend the committee adopted 13 pounds as the probable average future consumption of manganese per ton of steel. Information now available indicates that this figure should be about 14 pounds. The evidence points strongly to the fact that only a very small amount of the manganese derived from manganiferous iron ores reaches the steel ingot.

Recovery of Manganese in Basic Pig-Iron Practice

About 75 percent of the manganese in the charge is recovered in the metal in basic pig-iron practice. The amount of retained residual manganese in basic open-hearth steel depends very largely upon the extent to which plant practice favors a high percentage of MnO and a low percentage of FeO in slag at the end of the heat. The percentage of manganese in the slag depends upon the silicon in the metal, the silica content of the iron ore, any other factors that influence the slag volume, the percentage of manganese in the metal, and the proportion of iron and scrap. The FeO in the slag depends upon the amount of ore added and upon the slag volume. Manganese is eliminated during the early part of the heat; therefore, if a part of the slag is run off before the heat is finished the percentage of MnO in the finishing slag and the residual manganese will be low. Kinney (204) has published a chemical balance of an open-hearth heat made under conditions which favored high residual manganese. The steel at tapping contained 0.4 percent manganese,

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which represented 27.6 percent of the manganese charged. Pazetti (297) reports a month's practice using pig iron containing 1.65 percent manganese and no run-off slag. The residual manganese averaged 0.32 percent. He states further:

> In a plant using run-off slag, the record of five carefully observed heats showed average residual manganese to be 0.09 percent when the average manganese in the pig iron was 1.69 percent.

It is obvious that under some conditions virtually all the 150,000 tons of manganese derived in recent years from manganiferous iron ore found a resting place either in blast-furnace slag heaps or in those obtained from open-hearth furnaces. Hoyt (169), in discussing the effect of the use of manganiferous iron ores on manganese requirements, states:

> Present data indicate, unfortunately, that no material decreases in the amount of manganese required and no material increase in the recovery of manganese in the additions may be expected, so that the advantages are derived not from a decreased consumption but from the form in which it can be added.

Data on the increased quantity of manganese derived from manganiferous iron ores and the small changes in the manganese added as ferromanganese and spiegel from 1911 to 1929 confirm this viewpoint. Commercial expediency determines the practice which will prevail in individual plants. It appears that, in general, benefits due to secondary causes, such as slag fluidity and sulphur elimination, rather than those derived from residual manganese have been responsible for the use of high-manganese basic pig iron.

Desirability of Manganese in Basic Pig-Iron Practice

Sulphur control belongs essentially to the blast furnace. It can be eliminated in the open-hearth furnace by the use of additional limestone or ferromanganese, but both methods are costly and uncertain. Manganese in the charge aids in eliminating sulphur in the blast furnace. Herty and Gaines (153, 154) have shown the underlying cause for further elimination of sulphur by manganese during the time the metal is in the transfer ladles between the blast furnace and the open-hearth mixer. Wheaton (391) investigated the decrease in sulphur during the transfer of high-manganese basic pig iron from the blast furnace to the open-hearth mixer. His results follow:

	Manganese blast furnace, percent	Sulphur at blast furnace, percent	Sulphur at open-hearth mixer, percent
Average, 29 tests,	1.39	0.0867	0.041
Average, 89 tests,	1.72	.070	.035
Average, 26 tests,	2.13	.073	.031

Smith (350) states that high-manganese pig iron has the following advantages in the blast furnace: Increased rate of driving; high bottoms reduced; less runner and ladle scrap; higher blast temperatures possible;

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lower fuel consumption; less flue dust; and elimination of sulphur. He also states that irregular content of manganese in the ore (including iron ore) shipped is a disadvantage due to irregular content of manganese in the pig iron. Excessive percentages of manganese may also lead to breakouts due to low bottoms and corrosion of brickwork.

In open-hearth practice, advantages and disadvantages were given as follows: Advantages--sulphur elimination, improved quality of steel, ferromanganese saving, less lime and fluorspar, and increased tonnage; disadvantages--higher metallic losses and increased lining corrosion.

It has been rather generally assumed that residual manganese protects the steel against oxidation. Herty (150) states:

> Residual manganese does not serve as a protector against oxidation of the metal. Since the concentration of MnO in the metal depends on the concentration of MnO in the slag, it is possible to have the same concentration of FeO in the metal with 0.1 percent manganese as with 0.4 percent manganese, provided only that the concentration of MnO in the slag is four times as high in the second case as in the first. High residual manganese may denote a bath low in iron oxide, but the low iron oxide is the agent and not the result of high residual manganese.

The advantages of high-manganese, basic open-hearth charges, as given by Herty, are: (1) Increased fluidity of the slag, enabling a more basic slag to be carried, and increased speed of working; (2) increased ratio of MnS to FeS in the metal, giving the final addition of manganese a better chance to eliminate sulphur; and (3) decreased additions of ferromanganese.

Producers of manganiferous iron ores have noticed a decrease in the demand for this type of ore. Records, compiled by the Lake Superior Iron Ore Association, show that in 1927 the tonnage of manganiferous iron ores amounted to 4.6 percent of the total ore shipments from the Lake Superior district. In 1930, this figure was 3.6 percent, a decrease of about 22 percent. Some plants have found that alkali additions to the ladles give them the necessary control over sulphur. More extensive use of basic open-hearth slag has also lessened the demand for manganiferous iron ores.

THREE-STEP PROCESS FOR PRODUCING FERROMANGANESE FROM MANGANIFEROUS IRON ORES

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Due to their size, accessibility, and state of development the manganiferous iron ore deposits of Minnesota have attracted attention as a potential source of manganese. Zapffe (405) states:

> The Cuyuna district has a reserve tonnage of ore of 44,000,000 tons. If it averages 9 percent in manganese as the ore produced at present, it has a reserve of 3,960,000 units (tons of metallic manganese).

The United States Bureau of Mines has investigated the feasibility of producing ferromanganese from manganiferous iron ores containing 6 to 10 percent manganese, 40 to 45 percent iron, and 0.2 to 0.3 percent phosphorus. The ore was first smelted in an experimental blast furnace from which high-phosphorus spiegel (12 to 15 percent manganese and 0.5 percent phosphorus) was obtained. In the second step the spiegel from step 1 was treated in a small basic-lined converter, small open-hearth furnaces, and small electric furnace to separate the manganese from the phosphorus and the iron. The object was to obtain the manganese in the form of slag containing manganese, iron, and phosphorus in such proportions that the slag could be used as an artificial manganese ore. In the third step the high-manganese slag from step 2 was charged into the experimental blast furnace and converted into ferromanganese. Photographs of the furnaces used, arranged as a flow sheet, appear in figure 28. The small converter is not shown with the open-hearth and electric furnaces used in the second step because it proved unsatisfactory for separating manganese from the phosphorus and the iron.

Blast-Furnace Tests

In present practice, brown manganiferous iron ores are mixed with iron ores to produce basic pig iron. There was some question whether the manganiferous iron ores could be smelted by themselves due to high alumina in proportion to silica and high moisture content. Inasmuch as metal was needed for investigating subsequent steps of the process, it was decided to produce the metal from the ore rather than make it up synthetically from spiegeleisen ferrophosphorus, and pig iron. The cost of smelting these ores on an industrial furnace scale was prohibitive; therefore an experimental blast furnace was developed partly for this problem and partly for investigating problems fundamental to the production of pig iron.

A detailed description of the experimental blast furnace and the results of the test have been published (187). The furnace was operated continuously for about 1 month without any difficulties. Over 300 tons of ore were put through the furnace in producing about 130 tons of metal containing 12 to 15 percent manganese and 0.55 percent phosphorus. Rather than attempt to select an average or typical ore, material unusually high in alumina and moisture was chosen. Many Cuyuna ores which would produce slags in the normal range of 10 to 15 percent alumina present no smelting problem. Slag containing from 0.4 to 21 percent alumina was produced. A study of 278 slag samples showed that, as a whole, the effect of alumina was not very pronounced. If the alumina content of the slag was low, manganous oxide in the slag fell off more sharply as the basicity ($\frac{CaO}{SiO_2}$) increased than when the alumina was high.

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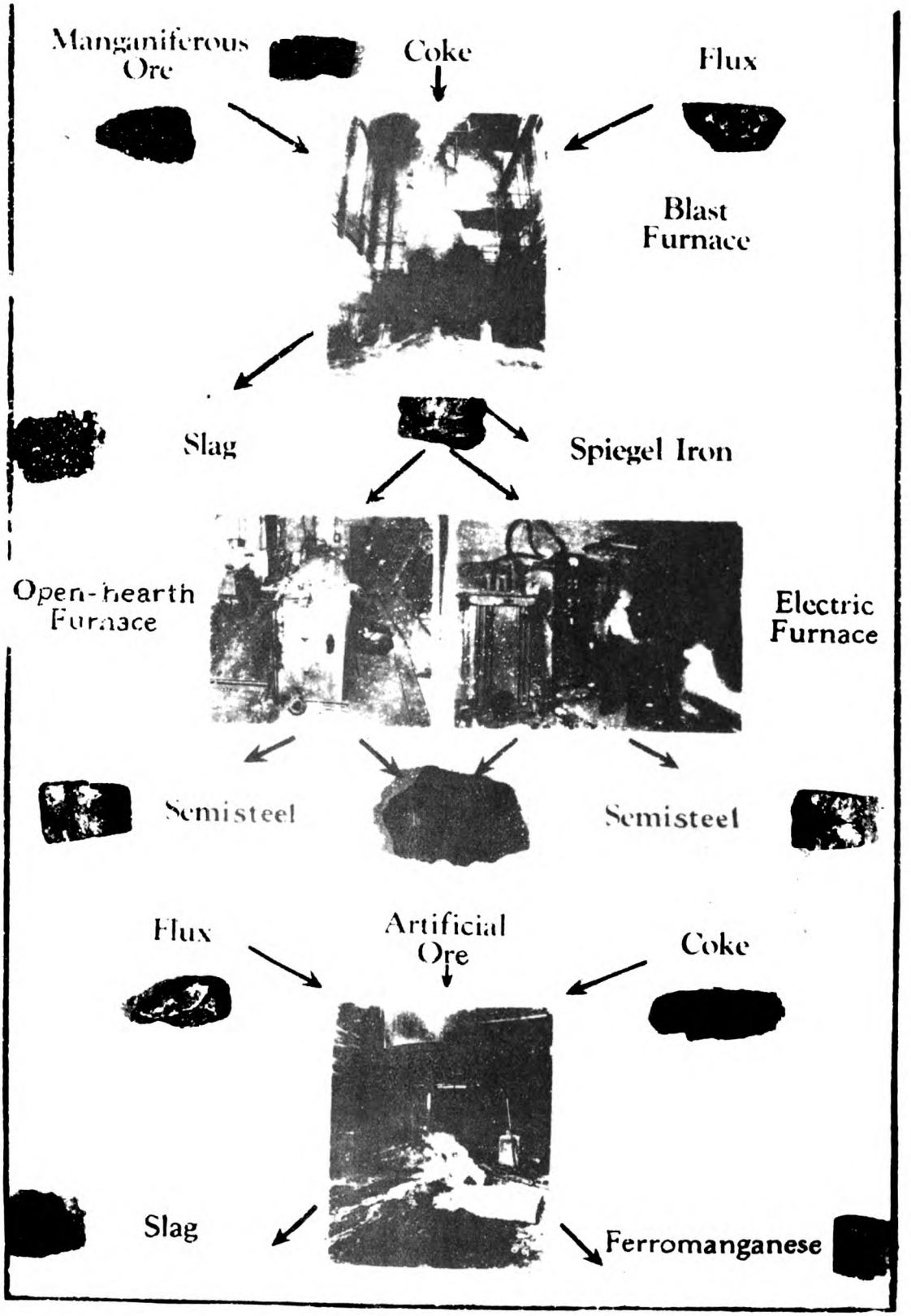

Figure 28.- Furnaces, raw materials, and products used in producing ferromanganese from manganiferous iron ores.

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General data from the operation of the furnace are given in table 76. The furnace, in general, operated uniformly, and the stock settled regularly with no slip or top explosions which may be aggravated by the generation of large amounts of hydrogen in the top of the furnace. Percentage of hydrogen in the top gas averaged 2.23, which was not unusually high. There should be no difficulty in smelting the brown ores in industrial furnaces with an 80 percent recovery of manganese and a fuel consumption of 2,500 to 3,000 pounds of coke, depending upon the grade of coke, particular ore used, facilities for heating the blast, and practice in general. Careful grading of the ore to a uniform analysis would be essential to regular blast-furnace operation.

The manganiferous iron ores to which this process will apply contain about 50 percent iron plus manganese and 50 percent oxygen plus moisture and gangue. By eliminating the oxygen, moisture, and gangue in the blast furnace the manganese is increased from 8 percent in the ore to about 15 percent in the metal, and the iron is increased from about 40 to 80 percent. The percentage of phosphorus is also approximately doubled, increasing from 0.25 in the ore to about 0.5 in the spiegel. An alloy containing manganese, phosphorus, and iron in these proportions is not a commercial product, due chiefly to the high phosphorus. By separating the manganese from the phosphorus and the iron two usable products may be obtained; one, a high-manganese slag suitable for producing ferromanganese, and the other, a low-silicon and low-sulphur carbon-iron alloy that can be further refined into steel.

Newton (274) discussed the possibilities of treating manganiferous iron ores by duplex processes. Manganiferous iron ores high in phosphorus would first be converted to high-phosphorus spiegel in the blast furnace. It was proposed to blow this high-phosphorus spiegel in a basic Bessemer converter to convert the manganese into a slag which would be poured off before it was contaminated by phosphorus. Phosphorus was to be eliminated after the manganese in order to produce steel. This proposal was tested experimentally with the small side-blown converter shown in figure 29.

Results Obtained in Blowing High-Phosphorus Spiegel

Eleven blows were made on molten spiegel with equally unsatisfactory results in each blow. The blows were "sloppy", much slag being thrown from the converter. It was difficult to regulate the blast due to the large amount of slag produced. As shown in figure 30, the manganous oxide ranged from 60 to 65 percent during the first 12 minutes of the blows and then decreased to about 50 percent. Manganese was eliminated faster than phosphorus, but prohibitive amounts of the latter were thrown into the slag. The ferrous oxide in the slag ranged from 20 to 30 percent or was equal to one half to one third of the manganous oxide present. Manganese cannot be separated from phosphorus and iron to the degree required in producing artificial ferro-grade ore by differential oxidation in a Bessemer converter. A high-phosphorus alloy containing about 60 percent manganese could probably be made from basic converter slag resulting from bessemerizing high-phosphorus spiegel. The results in the small converter confirmed reported data (188) on two spiegel blows by Waterhouse in an acid-lined, bottom-blown, industrial converter. The slag from the large converter contained about three times as much manganese as iron. Since the objective was to obtain slag containing about ten times as much manganese as iron, no further converter tests were made.

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TABLE 76. - General Data from Operation of Experimental Blast Furnace

	Period No. 1	2	3	4	5	6	7	Average
1. Ore ..... lb. per ton	6,547	6,015	5,460	5,831	5,704	5,628	6,472	5,922
2. Stone ..... do	2,078	1,344	1,456	1,039	1,407	1,398	1,312	1,413
3. Coke ..... do	3,805	3,707	4,368	3,594	2,961	3,106	3,162	3,391
4. Carbon ..... do	3,289	3,224	3,887	3,211	2,442	2,547	2,657	2,891
5. Metal per day..... tons ..	3.67	3.97	3.43	4.22	5.18	4.92	4.72	4.41
6. Slag ..... lb. per ton	2,248	2,414	2,264	1,918	2,255	2,119	2,145	2,225
Ore analysis (nat.) .. percent								
7. Manganese	8.13	7.66	8.93	8.16	8.31	8.56	8.28	8.24
8. Iron	33.41	33.98	32.76	32.29	33.59	34.20	35.15	33.78
9. Silica	8.40	8.19	9.31	5.57	10.26	7.94	4.58	8.12
10. Alumina	6.45	6.64	6.01	5.98	5.23	6.14	6.25	5.98
11. Phosphorus	.26	.25	.27	.27	.25	.25	.27	.26
12. Moisture	15.93	16.21	16.84	21.36	16.50	16.85	18.28	17.13
13. Loss on ignition	9.65	9.00	10.17	10.45	9.94	10.08	11.38	10.03
Metal analysis ..... percent								
14. Carbon	4.71	4.48	4.67	4.74	4.60	4.67	4.26	4.57
15. Manganese	11.97	11.96	15.33	13.82	11.44	13.05	10.96	12.23
16. Silicon	.14	.34	.52	.22	.23	.14	.12	.24
17. Phosphorus	.59	.59	.61	.57	.51	.47	.53	.55
18. Sulphur 1/								
Slag analysis ..... percent								
19. Lime	40.24	33.81	38.34	33.88	37.75	39.64	36.28	36.97
20. Alumina	14.25	17.40	16.44	17.70	12.27	13.24	16.59	14.90
21. Silica	28.28	32.39	31.68	30.83	33.21	31.17	27.16	31.27
22. Manganese oxide	12.13	13.01	10.33	13.68	12.08	12.58	14.76	12.64
23. Ferrous oxide	1.78	1.38	.79	1.09	1.21	1.88	3.33	1.61
24. Basicity $\left(\frac{CaO}{Al_2O_3 + SiO_2}\right)$	.95	.68	.80	.70	.83	.90	.83	.81
25. Mn charged ..... lb. per ton	532	461	488	476	474	482	536	488
26. Mn to metal ..... percent	50.5	58.0	70.4	65.2	54.1	60.7	45.7	57.7
27. Mn to slag ..... do	46.7	45.4	33.9	35.4	40.2	38.2	39.0	39.5
28. Mn unaccounted for 2/, do	2.8	+ 3.4	+ 4.3	+ .6	5.7	1.1	15.3	2.8
Temperatures								
29. Blast ..... °F.	530	553	575	521	608	662	581	576
30. Top ..... do	835	704	906	696	446	539	535	666
31. Tuyère ..... °C.	1644	1676	1724	1693	1696	1716	1683	1689
32. Slag ..... do	....	....	....	1335	1342	1476	1500	1413
33. Metal ..... do	1370	1328	1342	1352	1313	1331	1406	1349
34. Blast pressure .....in. of Hg.	5.64	5.35	4.72	4.48	5.25	5.48	4.79	5.16
35. Blast pressure..lb. per sq. in.	2.77	2.63	2.32	2.20	2.46	2.69	2.35	2.54
36. Air per minute 3/ ..... cu. ft.	569	605	637	626	589	589	607	601

1/ Below 0.01 in all periods except No. 5, where three casts ran 0.02, rest below 0.01.
2/ Plus sign indicates an excess recovered over that charged.
3/ Calculated from carbon burned at tuyères and top-gas analysis.

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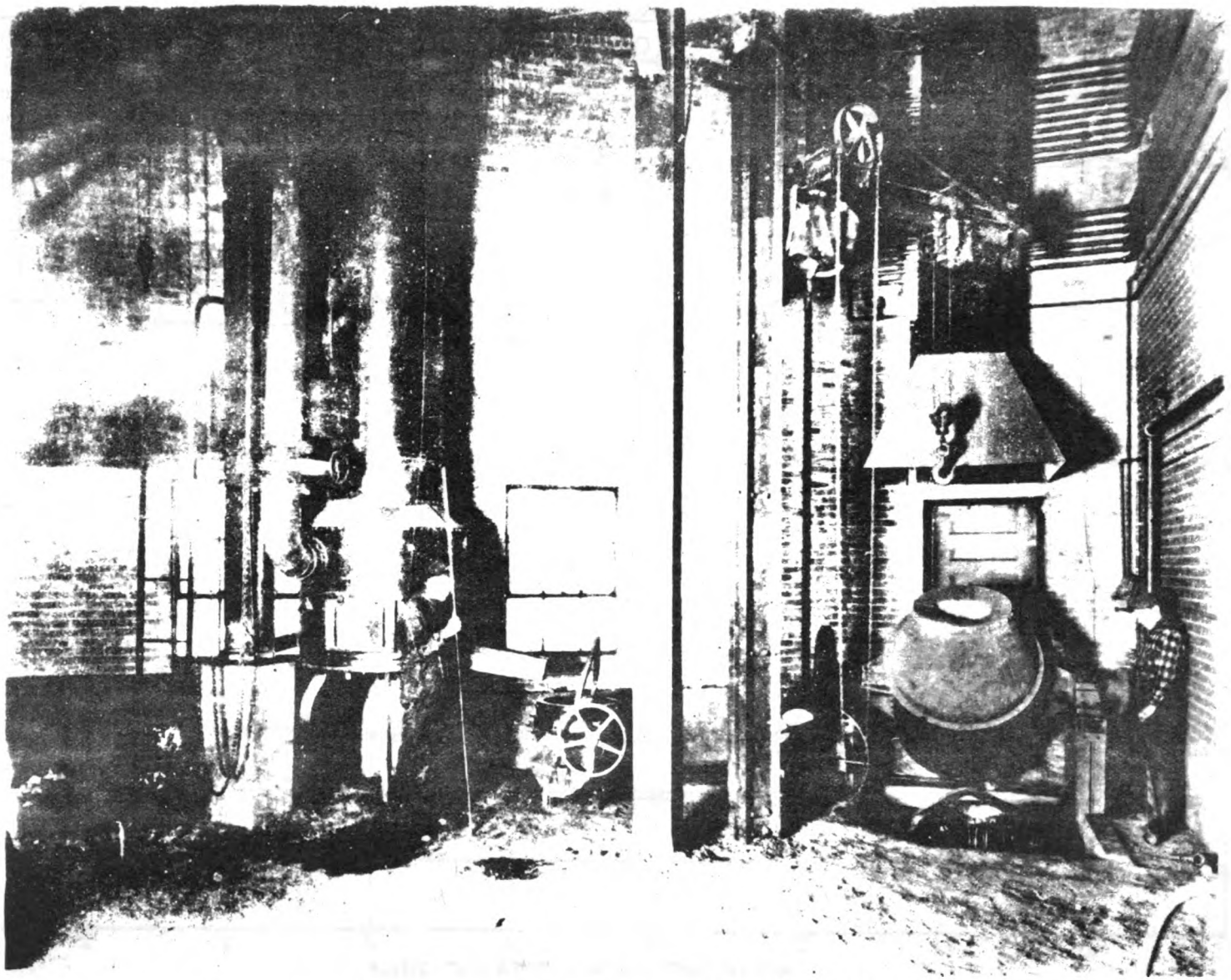

Figure 29. - Cupola and experimental side-blow converter.

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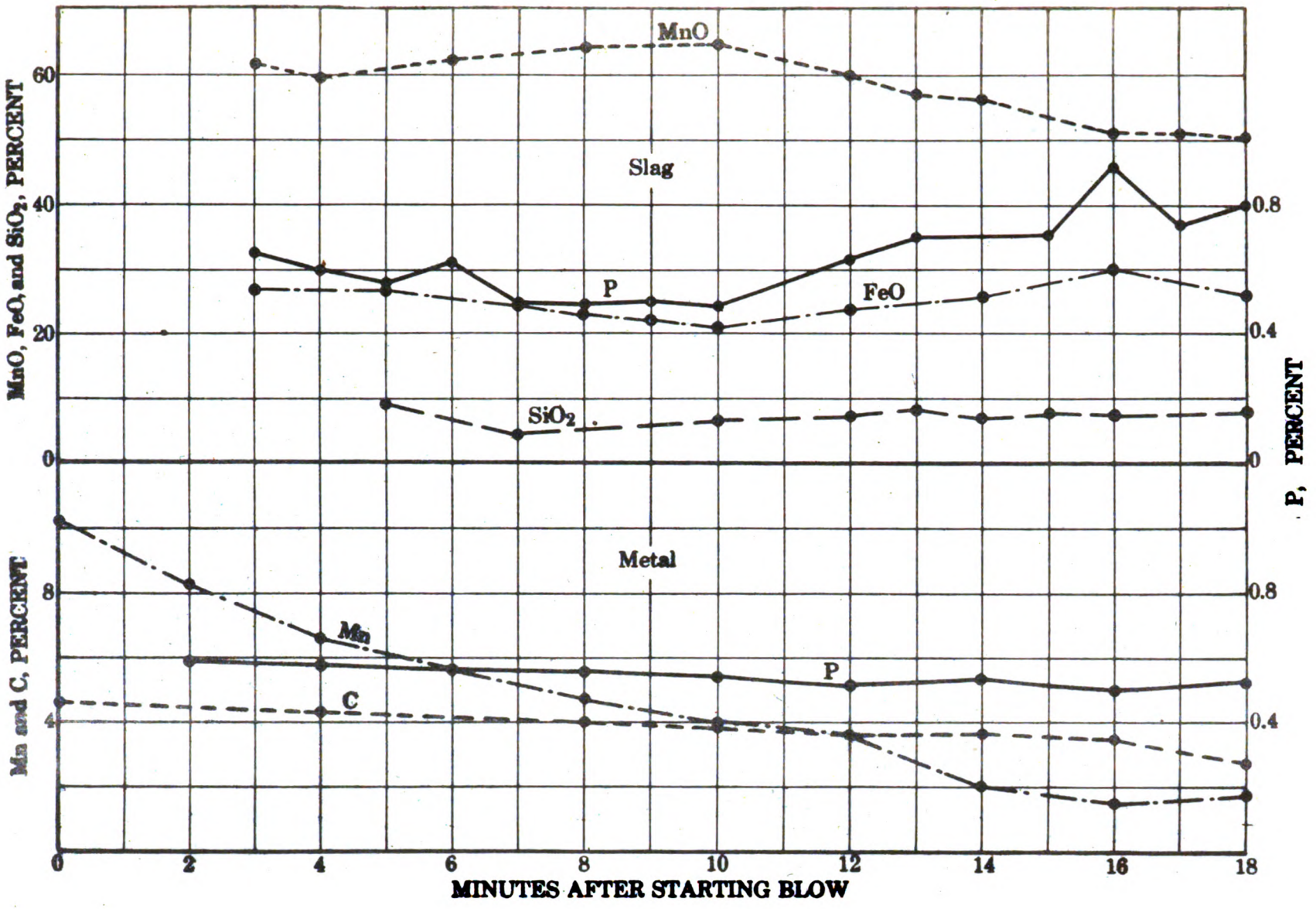

Figure 30.- Average change in slag and metal for 11 converter blows.

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Tests in Acid-Lined Open-Hearth Furnace

Attempts were made to separate the manganese from the phosphorus and iron by oreing down charges of molten spiegel in a small acid-lined open-hearth furnace. The results were very unsatisfactory due to corrosion of the lining by the manganese and to prohibitive amounts of phosphorus, ferrous oxide, and silica in the slag. The acid slag contained as much as 1.5 percent phosphorus. Phosphorus is not thrown into the slag in acid open-hearth practice because such a small amount is present. Since the acid lining did not solve the phosphorus problem tests were made with a basic lining.

Tests in Basic-Lined Open-Hearth Furnace

The difficulty of excessive corrosion of the furnace lining encountered in the acid open hearth was corrected by the use of a magnesite lining. This change in refractory lining did not solve the problem of producing slag containing about ten times as much manganese as iron and less than 0.2 percent phosphorus. If 4 or 5 percent manganese was left in the metal a proper ratio of manganous oxide to iron oxide in the slag could be obtained. Such amounts of manganese represented about one third of all of the manganese in the spiegel, so that such a procedure was not satisfactory.

The process was slow because with small ore additions a very thick slag was soon formed, and further action took place at an extremely slow rate. It became obvious that to eliminate the manganese rapidly and to get it down to 0.5 percent or under it was necessary to treble the amount of iron ore added. The fluid slag and high concentration of ferrous oxide forced the following reaction rapidly to the right, $FeO + Mn = MnO + Fe$.

The next problem was that of properly adjusting the ferrous oxide and phosphorus in the slag. Differences in the relative reducibility of ferrous oxide, phosphorus compounds, and manganous oxide suggested a means of adjusting the iron and phosphorus. Ferrous oxide reduces rapidly at 950° C. At somewhat higher temperatures (1,100° to 1,200°C.), phosphorus compounds are reduced, but it requires a temperature of about 1,400° C. and highly-reducing gases to deoxidize manganous oxide rapidly. Experiments showed that a 2- to 3-inch layer of small coke spread over the surface of the slag protected it from the oxidizing furnace atmosphere and provided condition under which the ferrous oxide and ferrous phosphate in the slag were reduced with a comparatively small reduction of manganous oxide.

Most of the experimental work on producing an artificial manganese ore from high-phosphorus spiegel was performed in the small tilting open-hearth furnace shown in figure 28. Tests with a small electric furnace showed that furnaces of this type have some distinct advantages over open-hearth furnaces for this particular operation (see p. 233. The procedure, which was essentially the same in both types of furnaces, can best be explained by following the progress of a typical open-hearth heat, shown in figure 31.

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The furnace was first charged with 500 pounds of cold spiegel containing 15.75 percent manganese. If the process were conducted on an industrial scale the hot metal would be transferred directly from the blast furnace to an open-hearth or electric furnace. It was necessary to start with cold metal in most of this experimental work. Iron ore was added 2 hours after charging. As the manganese in the metal and the ferrous oxide in the slag decreased, the manganous oxide in the slag increased as a result of the following reaction,

$$Mn \text{ (in metal)} + FeO \text{ (in slag)} = MnO \text{ (to slag)} + Fe \text{ (to metal)}.$$

Two and one-half hours after the ore was added or 4-1/2 hours after charging, the metal contained less than 0.5 percent manganese. The slag at that time contained 55 percent MnO, 30 percent FeO, and about 0.7 percent P. Coke was then added to adjust the phosphorus and the ferrous oxide in the slag. After holding the bath under a 2- to 3-inch layer of 1/4- to 1/2-inch coke for 2-1/2 hours the ferrous oxide was reduced to 6 percent. Meanwhile the manganous oxide had increased to 66 percent, which provided a 11:1 ratio of manganese to iron. The results of a great many heats show that the necessary adjustment of phosphorus in the slag occurs simultaneously with the reduction of ferrous oxide.

Detailed information on important features of experimental work in small open-hearth and electric furnaces has been published in several progress reports (139, 190) and a summary report (188). The important features of the work include the amount of ore added, composition of the slag, recovery of manganese, time required for operation, amount and composition of metal produced, and comparison between electric and open-hearth furnaces.

Composition of Slag

Results with small open-hearth furnaces indicate that two types of slag can be made. By using silica to maintain slag fluidity, slags can be produced containing 16 percent SiO_2, 65 to 70 percent MnO, 6 percent FeO, 0.16 percent P, 7 percent Al_2O_3, and a few percent MgO and CaO. The silica in the slag may be less than 10 percent, provided enough alumina is present so that the sum of the two constituents ranges from 19 to 23 percent. A typical slag in which part of the silica has been replaced with alumina would contain 65 to 70 percent MnO, 6 percent FeO, 0.16 percent P, 10 percent SiO_2, and 13 percent Al_2O_3. The amount of silica and alumina necessary to obtain a workable slag will depend upon the temperature and the advantage to be gained from shortening the time required for a heat.

Recovery of Manganese in Basic Open-Hearth Heats

The analysis of dust collected from metered portions of flue gas showed that about 1 percent of the manganese and 1.5 percent of the iron charged as spiegel were lost as dust. The ratio of manganese to iron in the dust samples was about the same as in the spiegel, indicating that the dust was produced by oxidation of the surface of metal globules thrown into the gas stream by the mechanical action of the bath. Samples of dust removed from blades of the exhauster and from the flues also contained manganese and iron in about the same ratio as the two occurred in the spiegel treated.

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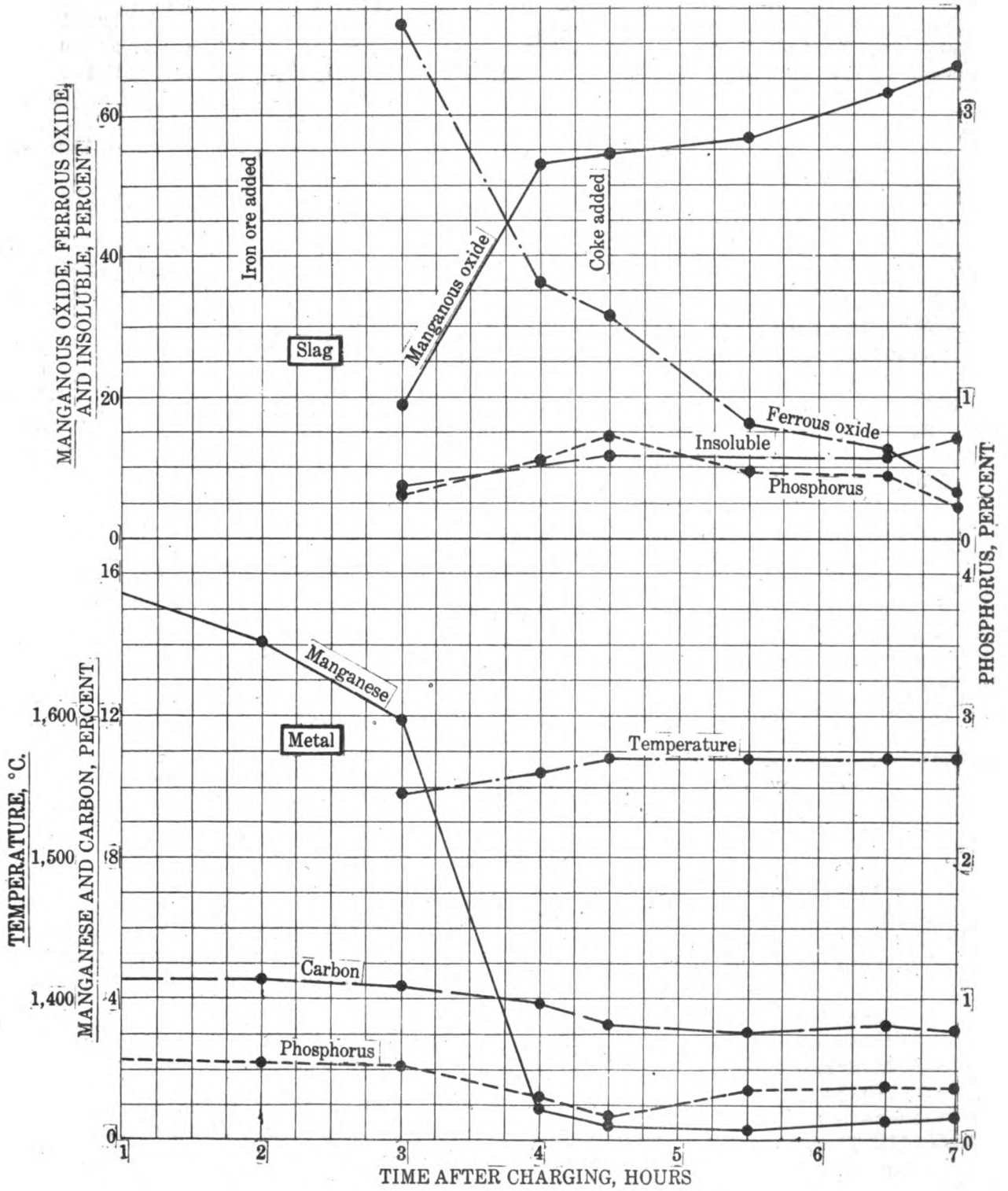

Figure 31.- Changes in composition of slag and metal in heat 437.

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The data obtained from dust samples indicated that the loss of manganese by volatilization was small. This was confirmed by manganese balances on 200 open-hearth heats, which showed an average recovery of 85 percent of the manganese in the slag and 10.3 percent in the metal, leaving a loss of 4.7 percent.

Time Required for a Heat

The time required to recover the manganese in high-phosphorus spiegel in the form of a slag suitable for producing ferromanganese is governed largely by the length of time required to adjust the phosphorus and ferrous oxide in the slag. From 95 to 98 percent of the manganese was oxidized in an hour when the weight of iron in the ore addition was about 1.5 times the weight of manganese in the spiegel. The time required to adjust the phosphorus and the iron in the slag ranged from 1 to 3 hours. If the slag was fluid, the reduction of FeO and of $(FeO)_3P_2O_5$ was rapid, provided the slag was completely covered with coke and was at a temperature of 1,575° to 1,600° C. If the slag was viscous the adjustment of phosphorus and iron was slow and erratic. From 4 to 5 hours would probably be required for the complete operation in an industrial furnace.

COMPOSITION OF METAL PRODUCED

Approximately 1 ton of metal was produced for each ton of spiegel treated. The average analysis of metal produced in 16 typical heats was: Manganese, 0.87 percent; phosphorus, 0.43 percent; carbon, 3.4 percent; Sulphur, 0.002 percent; and silicon, 0.011 percent. In practice this metal would be refined into steel by the normal basic open-hearth process. The high-phosphorus content would be a detriment, but the extremely low sulphur content would be an advantage. Only through the value of this metal can the operation of recovering manganese from high-phosphorus spiegel be economical. The high-manganese slag should be regarded as a byproduct incidental to the production of steel from manganiferous iron ores.

Electric-Furnace Tests

High-phosphorus spiegel was treated in two stages, in the electric furnace and in the open-hearth furnace. The first stage was conducted under oxidizing conditions and the second under reducing conditions. Final adjustment of the slag was made in the last stage under reducing conditions.

The electric furnace has a decided advantage over the open-hearth furnace due to the more strongly reducing atmosphere that can be readily established. As a result of this advantage it required about one half as long to make heats in small arc furnaces as it did in the small open-hearth furnaces. In general, electric furnaces were more flexible than open-hearth furnaces. Being able to skim the slag manually from an industrial, circular electric furnace would be an advantage because slag lower in silica and alumina could be produced. Due to the shorter time required for the operation in the electric furnace it appears that the cost of treatment would be comparable to the cost of treatment in open-hearth furnaces.

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Refractory Lining

A magnesite lining was satisfactory in both the open-hearth and electric furnaces. The bottom and sides tended to build up rather than to cut out.

Mineral Composition of Slags

The composition of the final slags in these tests is in that portion of the ternary system MnO-FeO-SiO_2, proposed by Herty, Conley, and Royer (158), in which MnO is the major slag constituent. In the field adjacent to this knebelite (orthosilicate of Mn and Fe) is the major slag constituent. As a result of a rather preliminary petrographic study, McCaughey stated:

> These slags are composed essentially of two minerals, manganosite and knebelite. In spite of the fact that the manganosite exceeds the silicate mineral in large amounts, the latter is the continuous phase and has crystallized out in fairly large crystals enclosing the manganosite.

Silicates of various metal oxides are reduced with more difficulty than oxides. It is important to note therefore that these slags are composed primarily of MnO and not of the silicate of manganese.

Production of Ferromanganese from Artificial Manganese Ore

In producing slag containing 65 to 70 percent MnO and about 6 percent FeO from high-phosphorus spiegel, it is necessary to add a thinning agent or flux to obtain a degree of slag fluidity conducive to practical reaction rates. Herty, Conley, and Royer (158) found from tests on a crucible scale that alumina has a thinning effect upon high-manganese slag. They suggested its use in the production of high-manganese slag. Tests in a small open hearth and a small electric furnace showed that alumina could be used as a thinning agent. As stated on page 232, two types of slag can be made; one containing 16 percent SiO_2 and 4 to 6 percent Al_2O_3, and another containing 8 to 10 percent SiO_2 and 10 to 12 percent Al_2O_3. Although the high-silica slags appeared to be somewhat more fluid, satisfactory results were also obtained when using alumina as a thinning agent. Before drawing any conclusions, however, about the use of alumina as a substitute for part of the silica, it was necessary to investigate the smelting characteristics of the two types of slag.

Blast-furnace slag produced in smelting manganese ores normally contains about twice as much silica as alumina. If high-manganese slag, fluxed with alumina, were used as a manganese ore, the blast-furnace slag would contain about equal amounts of silica and alumina. Such a proportion of silica and alumina is rarely found in blast-furnace slag.

In producing pig iron the operator adjusts the slag composition to meet sulphur and silica specifications in the metal. In producing ferromanganese operators strive to adjust the slag so as to promote the complete reduction of manganous oxide. The slag in the crucible of a ferromanganese furnace

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contains a series of compounds composed of CaO, MgO, SiO_2, and MnO. In what manner or to what extent the proportion of silica and alumina changes the ease and completeness with which manganous oxide can be reduced from slag under blast-furnace conditions is not known. Herty, Conley, and Royer found from reduction tests in graphite crucibles at 1,550° C. that high-alumina slags reduced as readily as the high-silica slag.

For lack of a better working rule operators base the requirements for dolomite and calcite upon the amount of silica in the charge. Enough fluxing stone is added so that the sum of the lime and magnesia will be 1.5 to 1.9 times the total silica in the charge, including the coke ash. Bases are added to aid in the reduction of manganous oxide which is in solution in the slag and to limit the reduction of silica. Alumina is not reduced under blast-furnace conditions; therefore, the only question is whether basic oxides facilitate reduction of manganous oxide. If alumina in the charge can be ignored in calculating the amount of bases required to produce a slag from which manganous oxide can be reduced, it should be less objectionable than silica because of lower slag volumes. The effect of alumina upon pig-iron practice has been discussed, but no information appears to have been published on the effect of alumina on ferromanganese practice.

Tests in graphite crucibles by Herty, Conley, and Royer indicated that manganous oxide can be reduced satisfactorily from slag containing 40 percent CaO, 30 percent SiO_2, and 30 percent Al_2O_3 on a three-component basis. Such slag offers encouraging possibilities from the standpoint of slag volume because of the unusually low basicity.

In view of the amount of work which had been done on the first two steps of the method proposed for producing ferromanganese from manganiferous ores, it was decided that the smelting characteristics of the two types of slag should be investigated with the experimental blast furnace. Such a test seemed desirable as it would complete on a small-furnace scale the last of a series of three operations by which it was hoped an alloy containing 80 percent manganese could be produced from ore containing 8 percent manganese.

EXPERIMENTAL BLAST FURNACE AS A TOOL FOR INVESTIGATING SMELTING PROBLEMS

The daily capacity of the experimental blast furnace is about one half of 1 percent of a modern industrial furnace. The question arises as to what types of problems can be investigated with such a furnace and what significance can be attached to the results obtained. The brief resume of former experimental furnace tests will illustrate its field of usefulness.

Segregating ore into sizes and charging the sizes into an experimental furnace in sequence improved the operation very markedly and suggested that within reasonable limits uniformity of size in a given charge has more effect upon the rate and completeness of reduction than does the absolute size of the average particle.

Prompted by the general suggestion (325) that uniform particle size in each layer should be beneficial, one plant has been separating its ore into

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three sizes and charging each size separately for several years. This practice, by which production was increased 110 tons per day on foundry iron and 82 tons on basic iron with a corresponding coke savings of 488 and 437 pounds per ton, has been described by Kinney (205). Large variations in gas composition at various positions across several planes of the experimental blast furnace (327), forecast similar nonuniformity in full-size furnaces charged with bell and hopper, similar to the equipment used in the experimental furnace. Varying degrees of nonuniformity in temperature, in gas composition, and in gas velocity were found by Kinney (206, 207) in several industrial furnaces. Slags containing as high as 53 percent Al_2O_3 and as low as 6 percent SiO_2 have been melted and tapped without difficulty from the experimental blast furnace. The ease with which these slags were produced in the experimental furnace (185, 189, 191) left little doubt as to the possibility of producing in the blast furnace a slag similar in composition to the so-called high-alumina or quick-setting cements.

The experimental blast furnace is particularly useful in studying the smelting characteristics of new raw materials and in investigating ranges of slag composition outside of those of normal practice. The production of ferromanganese from two types of high-manganese slag presented a problem of this type.

The thermal requirements of the experimental furnace are vastly different from those of a large furnace due to large heat losses and low heat reserve of the little furnace below the tuyères. Experience on the small furnace shows that it requires 75 to 100 percent more fuel to do the same smelting work in the 1/2 percent unit as in the full-scale furnaces.

Raw Materials

Coke

Size of particle exerts a predominating influence upon the space required completely to convert atmospheric oxygen into carbon monoxide during the process of combustion. Normally, the oxygen and carbon dioxide are converted into carbon monoxide in localized zones extending 40 to 50 inches beyond the nose of the tuyères. If the coke particles range in size from 3/4 to 1-1/2 inches, the oxygen and carbon dioxide disappear in 18 to 22 inches. Byproduct coke, known on the market as "nut coke", was selected for the experimental blast-furnace test to minimize the size of the combustion zones and thus establish as strongly reducing conditions as possible in the hearth of the furnace. Typical percentage analyses of the coke follow:

Fixed carbon	Ash	Volatile matter	Sulphur	Ash			
				SiO_2	Al_2O_3	Fe_2O_3	CaO
90.67	8.38	0.95	0.53	- -	- -	- -	- -
92.30	7.37	.33	.55	- -	- -	- -	- -
91.93	7.59	.48	.42	35.21	27.2	28.22	6.12
91.37	7.81	.82	.57	35.72	29.6	28.33	3.12
91.00	8.00	.90	.50	37.10	26.0	26.00	6.20

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FLUXES

High-grade calcite and dolomite were used as flux. In place of the 4- to 6-inch pieces used in industrial furnaces particles ranging from 1/2 to 2-1/2 inches were used. The distribution of various sizes is given in table 77. About 90 percent of the pieces ranged in size from 0.5 to 2.5 inches. Car samples showed the following percentage composition:

	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3
Limestone	53.7	1.3	1.00	0.5	1.1
Dolomite	30.4	21.6	.80	.4	1.2

TABLE 77. - Screen Analyses of Raw Materials, Percent

Size	Coke	Calcite	Dolomite
-2.5 + 1.05 inches	76.5	52.1	46.7
-1.05 + .742 inch	21.0	28.6	32.7
- .742 + .525 inch	1.2	9.9	11.7
- .525 ..... inch	1.2	9.4	8.9

	Artificial ore no. 1 1/	Artificial ore no. 2 2/	Manganese ore no. 1	Manganese ore no. 2
-2.5 +1.05 inches	31.2	12.35	-	26.42
-1.05 + .742 inch	27.6	20.60	4.67	26.43
- .742 + .525 inch	18.2	14.45	6.54	14.95
- .525 + .371 inch	6.8	7.22	9.35	6.90
- .371 +3 mesh	4.9	9.28	11.20	4.60
-3 mesh +6 mesh	11.0	13.40	23.40	6.90
-6 mesh	-	22.70	44.84	13.80

1/ Silica higher than alumina. 2/ Alumina higher than silica.

High-Manganese Slags or Artificial Ores

Two types of high-manganese slag were used as a source of manganese. The greater part of the slag, which had been fluxed with silica, was produced by treating high-phosphorus spiegel in the open-hearth furnace. It was necessary, however, to make up virtually all of the high-alumina slag by remelting manganese ore in the open-hearth furnace and by adding bauxite as a source of alumina. The slag was tapped on top of a small amount of raw ore which aided in producing a more porous product.

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Screen analyses of the two types of slag are given in table 77. The high-silica slag contained virtually no material smaller than 6-mesh. About 85 percent of it ranged in size from 0.5- to 1.5-inch pieces. The slag which had been fluxed with alumina was smaller in size (minus 14 mesh) but contained virtually no potential flue dust. From the standpoint of physical structure, material of this type is very desirable. Percentage analyses of the two types of slag follow:

	Mn	Fe	SiO_2	Al_2O_3	P
Slag fluxed with alumina	42.1	4.47	9.4	13.7	0.19
Slag fluxed with silica	49.8	4.50	16.0	5.0	.20

The slags are similar chemically except that in the first case about 7 percent silica has been replaced with an equal amount of alumina.

Similarity Between High-Manganese Slags and Sinter

The idea of using a fused product in place of an ore is neither new nor novel. It was formerly believed that a comparatively small amount of fusion occurred in sintering and that the formation of iron silicate was regarded as being highly undesirable. Klugh (208) states that the formation of iron silicates is due to high temperatures and can be avoided by proper control of time and temperature. More recently Schwartz (345) has shown by a microscopic study of polished surfaces that sinters are predominantly and in most cases almost entirely composed of a new generation of crystals or grains and that bonding is due to the interlocking of magnetic grains and the binding together of such grains by iron silicate. Sinter has more desirable physical structure than most iron ores. Its reducibility compared with iron ores has been the subject of considerable discussion and speculation and but little experimental inquiry.

High-manganese slag consists of manganous oxide bonded with iron and manganese silicates. It contains a large number of openings or pores formed by the evolution of gas. As in the case of iron-ore sinter, its resistance to size degradation aids in producing a more open blast-furnace charge comparatively free from dust. Complete and final reduction of manganous oxide is not accomplished before fusion occurs in any case. The fact, therefore, that a manganese-bearing product has been fused would not seriously affect its reducibility.

Commercial Ores

Two commercial ores were used in making up the synthetic slags. These were also used in the experimental blast furnace for a short period. As shown in table 77, one of the ores was rather fine, while the other had been crushed to a size comparable to that of the high-manganese slags.

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Analyses of two ores, percent

	Mn	Fe	SiO_2	Al_2O_3	P
Manganese ore no. 1 ..	57.2	1.6	7.0	1.56	0.20
Manganese ore no. 2 ..	43.2	5.0	6.4	8.20	.19

These ores were not selected nor is their analyses reported with any implication that they are representative, commercial manganese ores. They were chosen primarily for convenience in making the synthetic slag.

DESCRIPTION OF EXPERIMENTAL BLAST FURNACE

A detailed description of the experimental blast furnace and of the plant layout has been published in a previous report (187). The dimensions and lines of the furnace are shown in figure 32. Normally, the weight of the slag is calculated. It was desirable to have more accurate information; therefore, the slag was caught in heavy cast-iron boxes. The ferromanganese and a portion of the slag were collected in one box and the overflow of slag in a second. This procedure avoided contamination of the slag by the ladle lining and permitted accurate weighing of the slag and the metal after removal from the boxes. In order to allow a longer time for reduction of manganese oxide in the crucible, the cinder notch shown on the left in figure 37 was not used, that is, the slag was not flushed from the furnace between casts. All of the slag produced was tapped with the metal at 3-hour intervals.

Discussion of Operating Results

Rate of blowing, slag viscosity, and burden or weight of raw material per unit of coke were factors for which there was no precedent or guide when the experimental blast furnace was blown in. It was necessary, therefore, to make a number of changes during the early part of the test. An air blast of 300 cubic feet per minute gave the best results. Faster rates of blowing led to increased slag losses, and at slower rates insufficient metal and slag were brought into the crucible to prevent the bottom of the furnace from building up. The slag and metal entering the crucible are the chief source of heat below the tuyère level. Experience with a number of small furnaces has shown that, unless the slag and metal are brought into the crucible at a sufficient rate to compensate for high heat losses and to provide a heat reserve below the tuyères, the crucible skull around the sides and the bottom of the furnace builds up.

Satisfactory operation of any furnace producing ferromanganese requires proper adjustment of slag basicity and of the amount of ore burden, which in this instance was high-manganese slag. The high-manganese slag, which had been fluxed with silica, was charged in the first half of the 30-day test (see p. 238 for analysis). By a series of changes in the burden and in slag basicity the manganese in the slag was reduced from 30 to 11.5 percent. Table 78 contains analyses of metal produced during the first part of the test.

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The percentage of dolomite and calcite was varied, but time did not permit any systematic study of the effect of magnesia when operating on a charge containing normal proportions of alumina and silica. Higher percentages of magnesia gave better results on the high-alumina charges.

The results of the 30-day test have been summarized in table 79. Periods 1, 2, and 3 give the results obtained on the high-manganese slag or artificial ore which had been fluxed with silica. The most satisfactory results were obtained during period 1. The manganese in the slag averaged 11.5 percent and the basicity 1.59. Due to the large amount of iron introduced in the coke, the metal averaged 76.5 percent manganese, 1.5 percent less than the lower limit of 78 percent set for ferromanganese. The fuel consumption means very little unless it is considered in connection with past experience with the small furnace. Obviously, a furnace with a capacity of one half of 1 percent is much less efficient thermally than a full-scale furnace. From the test in which 12 to 13 percent spiegel was produced in the experimental furnace and from other tests with the same and smaller furnaces, it appears that 1 ton of ferromanganese could be produced in a large furnace from the same slag, with a coke consumption of 5,500 to 6,500 pounds.

TABLE 78. - Analyses of First 20 Casts of Ferromanganese, Percent

Cast no.	Manganese	Silicon	Phosphorus	Carbon
1	77.0	0.05	0.41	6.5
2	79.5	....	....	...
3	82.8	.10	.43	6.4
4	82.5	....	....	...
5	81.6	.04	....	6.6
6	80.5	....	....	...
7	84.6	.11	....	6.2
8	82.3	....	....	...
9	83.4	.05	.41	6.5
10	82.0	....	....	...
11	80.3	.12	.42	6.6
12	84.9	....	....	...
13	87.9	.14	.43	...
14	83.1	....	....	...
15	77.71	.12	.43	...
16	78.4	....	....	...
17	80.7	.11	.28	...
18	78.4	.06	....	...
19	79.5	....	....	...
20	78.5	.10	....	...

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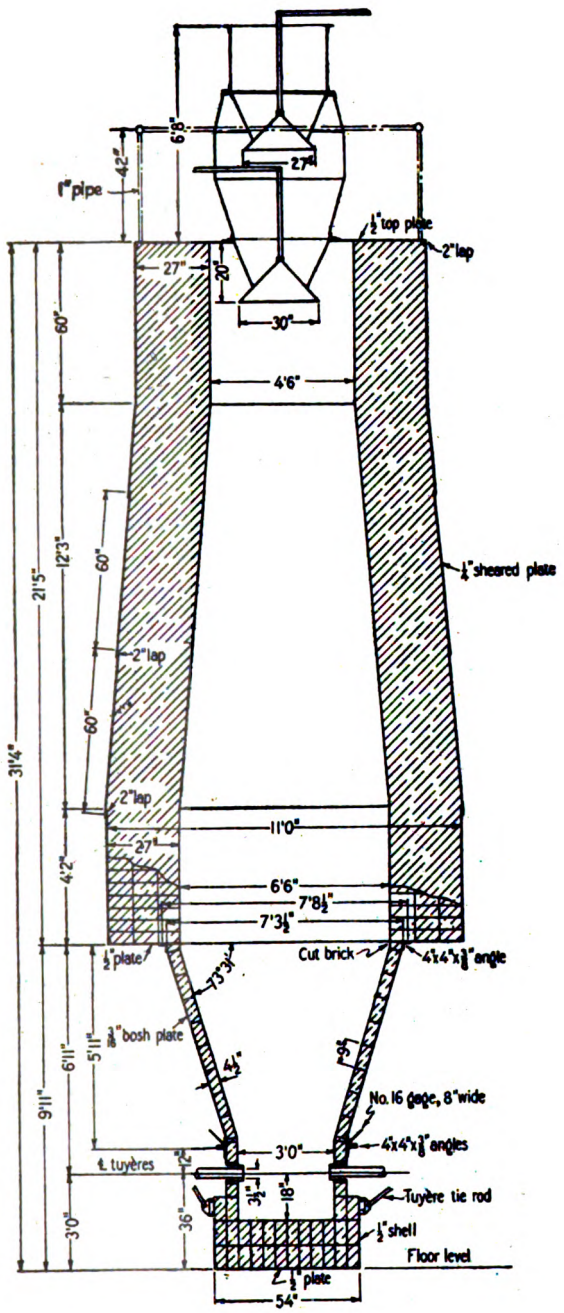

Figure 32.- Lines of experimental blast furnace.

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TABLE 79. - Operating Data of Experimental Blast Furnace During Ferromanganese Test

Item	Period			
	1	2	3	4
1. High-manganese slag ..... lb. per ton	4,540	5,250	5,070	6,800
2. Calcite ..... do	1,635	1,400	1,685	1,265
3. Dolomite ..... do	1,635	1,400	1,685	1,265
4. Coke ..... do	12,000	11,500	12,200	16,600
5. Carbon ..... do	9,800	9,400	10,000	13,500
6. Slag ..... do	4,350	4,558	5,258	6,400
Metal analyses, percent				
7. Manganese	76.5	74.0	74.0	73.0
8. Silicon	.1	.21	.12	.25
9. Carbon	6.5	6.5	6.5	6.3
Slag analyses, percent				
10. Silica	27.00	24.3	25.0	20.7
11. Alumina	11.65	10.7	11.0	17.7
12. Lime	31.80	23.7	28.5	19.0
13. Magnesia	12.15	9.1	11.2	6.2
14. Manganese	11.50	21.0	17.3	24.2
15. Basicity $\frac{CaO + MgO}{SiO_2}$	1.59	1.35	1.56	1.22
16. Manganese charged ..... lb. per ton	2,260	2,615	2,530	3,370
17. Mn to metal ..... percent	74.0	63.0	64.0	46.2
18. Mn to slag ..... do	22.0	36.0	36.0	44.0
19. Mn unaccounted for ..... do	4.0	1.0	.0	9.8
Temperatures				
20. Blast ..... °F.	930	860	942	720
21. Top ..... do	1,200	1,177	1,000	1,032
22. Tuyere ..... °C.	1,740	1,700	1,735	1,710
23. Slag ..... do	1,490	1,465	1,515	1,460
Pressure				
24. Blast ..... in. Hg.	1.3	2.1	1.3	1.1
25. Blast ..... lb. per sq. in.	.64	1.0	.64	.5
26. Air per min ..... cu. ft.	300	300	300	300

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There would be no difficulty in producing the standard 80-percent alloy because of the smaller amount of iron introduced with the coke ash. When a slag of lower iron content was used, it was possible to produce in the small furnace metal containing as high as 87.9 percent manganese (see table 78). The iron in the slag can be adjusted by varying the second step of the process by which the high-manganese slag is produced from high-phosphorus spiegel. With the fuel consumption that may be expected on full-scale furnaces, a ratio of manganese to iron of 10:1, that is, 80 percent manganese and 5 percent iron, would allow the production of the standard 78- to 82-percent ferromanganese.

Silicon and Phosphorus

The silicon in the metal produced in the experimental blast furnace was uniformly low and well under the 1 percent limit sometimes set for ferromanganese. It has been suggested that it would be difficult to control the silicon content of ferromanganese produced from high-manganese slag containing 15 to 16 percent silica. It is conceivable with a furnace operated primarily to produce tonnage and without due regard for recovery that control of silicon would present a problem when operating on high-manganese slag. The previous history of and the chemical composition and physical character of the raw materials used as a source of manganese have little bearing upon the reduction of silica from the slag below the fusion zone. With normal adjustment of basic fluxes and with fuel necessary to obtain a satisfactory recovery of manganese, there should be no difficulty in controlling the silicon in the metal.

The upper limit set for phosphorus in the slag was 0.2 percent, which would correspond to about 0.4 percent in the ferromanganese. Slag of lower phosphorus content (0.15 percent or under) could be produced. An addition of 14 pounds of metallic manganese in the form of ferromanganese containing 0.4 percent of phosphorus, would increase the phosphorus in the steel by 0.003 percent, which is about 0.001 percent more than is introduced when using an average grade of ferromanganese to make steel of average manganese content. Samples taken after making manganese additions and recarburizing often show a considerable increase in phosphorus content compared to samples taken from the furnace just before tapping. This increase of manganese is only partly due to the phosphorus introduced into the ferromanganese. A large part of the increase results from a kickback of phosphorus from the slag to the metal during the course of recarburization which establishes reducing conditions. Low phosphorus content is, no doubt, an aid in marketing ferromanganese, but its importance as an ingredient of this alloy has been overemphasized.

Although there are apparently no reasons why high-manganese slag could not be used alone in producing standard 80 percent ferromanganese, mixing with natural ores might be advantageous. The general practice is to mix various ores in proportions which give the best balanced mixture, physically and chemically.

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Basicity of Slag

The most satisfactory results were obtained on the experimental furnace when slag basicity, expressed as $\frac{CaO + MgO}{SiO_2}$, was about 1.6. A more basic slag was produced, but the increase in slag volume more than compensated for the decrease in percentage of manganese in the slag. The loss of manganese in the slag is determined by the weight of slag and the percentage of manganese it contains. Periods 2 and 3 (see table 79) show that a lower percentage of manganese in the slag does not necessarily mean a smaller loss of manganese in the slag. The manganese in the slag averaged 3.7 percent less in period 3 than in period 2, but the loss in the slag was the same for both periods. It was very evident during the course of the test that when the slag basicity exceeded 1.6 to 1.7 the slag reaching the tuyeres was extremely basic due to some 25 to 33 percent manganous oxide. At such times comparatively cold lumps of limestone and slag reached the tuyère unmelted. The distance between the tuyères and the zone of fusion is related to the free-running temperature of the slag. Slag with a low free-running temperature melts at a higher level in the furnace, which means that it will trickle down over a longer coke column before reaching the tuyères. Although the time is comparatively short the surface contact is large. The temperature-viscosity relations of the slag influence the degree of spreading or dispersion of the slag as it drops down through the coke column against the rising gas stream. Basic oxides tend, in general, to retard the fusion of systems containing large percentages of manganous oxide and comparatively small amounts of silica. They also increase the viscosity. Hence, an excess of basic oxides, desirable in the last stages of reduction of manganous oxide in the crucible of a blast furnace, may be detrimental to the reduction of manganous oxide in and above the tuyère level.

Recovery of Manganese

The best recovery of manganese was obtained during period 1 when 74 percent of the manganese charged was recovered in the metal and 22 percent in the slag, leaving 4 percent unaccounted for. The large loss occurred in the slag and was due primarily to the high slag volume, which amounted to 4,350 pounds per ton of ferromanganese. With a fuel consumption of 6,000 pounds of coke, which might reasonably be expected on a large furnace, the slag volume would be reduced to about 3,500 pounds. This is about 1,000 pounds more slag than is normally produced when using the usual grades of imported ores. The larger slag loss resulting from this additional slag volume would be compensated for by a smaller stack loss due to the elimination of dusting. Measurements of the dust in the exit gases indicated that less than 1 percent of the manganese charged was carried off in the top gas. Manganese balances on periods 1, 2, and 3 showed a stack loss of from 0 to 4 percent, which merely means that the loss was probably on the order of 2 percent. The large loss indicated in period 4 will be discussed later. A stack loss of 10 percent and a slag loss of the same amount is a common distribution of manganese in furnaces operating on natural ores. By eliminating practically all of the dust loss and restricting the stack loss to a few percent loss by volatilization, the total smelting loss would not exceed 20 percent even though the slag loss were greater than 15 percent. Restricting the slag loss to 15

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percent when producing 3,000 pounds of slag per ton of metal would require holding the manganese in the slag slightly under 10 percent. Such a degree of elimination of manganese from the slag is readily attained in good practice.

Fuel Requirements on High-Manganese Slag and on Natural Ores

More coke would be required to produce 1 ton of ferromanganese from high-manganese slag than from natural ores of lower silica content. Tonnage for a given furnace would be smaller because of higher fuel requirements and also due to the necessity of allowing greater time to realize the same degree of reduction of manganous oxide from the larger volume of slag.

The relation between slag volume and fuel consumption, reported by Royster to be 0.88 pound of carbon for each additional pound of slag, was discussed on page 210. On this basis, 1,000 pounds of additional slag per ton would require 880 pounds of additional carbon. Since 1 ton of ferromanganese can be produced from natural ores on a fuel consumption of 4,500 to 5,500 pounds of coke with normal blast temperatures, it seems reasonable to assume that the coke requirements in smelting high-manganese slag would range from 5,500 to 6,500 pounds.

Operating Temperatures of Experimental Blast Furnace During Ferromanganese Test

The calorized pipe stoves used to preheat the air placed a limit upon the temperatures to which the blast could be heated without burning out the pipe elements. Blast temperatures were therefore several hundred degrees lower than those usually maintained on industrial furnaces. Low blast temperatures were, no doubt, partly responsible for the high fuel consumption of the small furnace. Tuyère temperatures on the experimental furnace averaged 1,721° C. compared to 1,550° C. for full-scale ferromanganese furnaces. The temperature of the slag produced in the experimental furnace averaged 1,480° C. compared to 1,426° C. for industrial furnaces (see tables 73 and 79). It was particularly difficult to get accurate temperature measurements of the metal tapped from the experimental furnace, due to small casts and the short interval between the time when the metal was running freely and the time when the slag would start flowing. Metal temperatures, measured with an optical pyrometer, are often too high due to a small slag film on the surface of the metal. In general, the metal from the experimental furnace was cold. The lowest temperature observed was 1,325° C. Rapid dissipation of heat from the crucible of the small furnace is responsible for the large difference between the temperature at the tuyères and the temperature of the metal. This difference, amounting to 350° to 400° C., corresponds to a similar value of 175°C. for industrial furnaces.

The low metal temperature, shallow crucible, small heat reserve below the tuyères, and overlapping of combustion zones are the principal factors which make a small blast furnace inefficient in producing ferromanganese. When the furnace was producing about one half ton of ferromanganese per day the bottom of the furnace remained at about the same level, the furnace was

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easier to tap, and recoveries were higher. Important amounts of manganous oxide are, no doubt, reduced by contact between slag and metal. Larger quantities of hotter metal therefore aided in the recovery of manganese.

There is a marked change in reducing conditions in the tuyère zone and at lower levels. A shallow crucible does not provide enough storage space in which slag can be held under strongly reducing conditions.

Operation on High-Manganese Slag Fluxed with Alumina

The operation of the experimental furnace on high-manganese slag containing 49.8 percent Mn, 16 percent SiO_2, and 4.9 percent Al_2O_3, was much more satisfactory than the results obtained on high-manganese slag containing 52.1 percent Mn, 9.4 percent SiO_2, and 12.7 percent Al_2O_3. These two types of slag were very similar except for the ratios of silica to alumina, 3.3 and 0.74, respectively. The criteria for comparing furnace practice when producing ferromanganese are recovery of manganese, fuel consumption, and tonnage. By gradually adjusting slag basicity and the burden it was possible to produce from a high-silica charge slag averaging 11.5 percent manganese. With the prevailing slag volume, 74 percent of the manganese was recovered in the metal (see table 79, period 1).

When operating on a high-alumina charge the furnace did not respond to changes in slag basicity and the amount of fuel used. An effort was made during the course of 10 days continuous operation to get the manganese in the slag down to a reasonable figure. The best results and the only data which warranted summarizing and presenting in detail have been given in table 79, period 4. The manganese in the slag averaged 24.2 percent compared to 11.5 percent on the high-silica charge. Due to this high percentage of manganese 44 percent of the manganese was lost in the slag compared to a loss of 22 percent when operating on a high-silica charge. Only 46.2 percent of the manganese charged was recovered in the metal. About 10 percent of the manganese was not accounted for in the slag and metal. There are no apparent reasons for any greater volatilization loss or dust loss during the operation on the high-alumina charge. The slag produced during period 4 contained almost as much silica as alumina, whereas that produced during period 1 contained about 2.5 times as much silica as alumina. This difference in slag composition apparently affected the temperature-viscosity relations of the slag. The high-alumina slag contained considerable metal shot, ranging from 1/32 to 1/8 inch in diameter. In most cases these shot were concentrated in the lower part of the cold slag, which was collected in the same mold as the metal. This indicated that they were in suspension in the slag during tapping and settled out before the slag solidified after tapping. The poor separation of slag and metal indicated a difference in the physical properties of the slag. An effort was made to reclaim the larger shot, but there was an unavoidable loss of metal in the slag. Samples taken for chemical analyses were given a preliminary crushing and screened to remove shot which could not readily be removed, as they were feebly magnetic. Had it been possible to get a clean separation of slag and metal the recovery of manganese in the metal would probably have been about 5 or 6 percent higher, and the manganese unaccounted for would have been reduced to 4 or 5 percent.

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There was a decided tendency for the bottom of the furnace to build up when producing the high-alumina slag. It was often necessary to turn the tapping bar upward in order to reach the liquid metal. At times it was necessary to open a hole at a higher level. This operating difficulty, as well as the poor separation of slag and metal, might be less pronounced on a large furnace, but the same troubles would probably occur to a modified degree.

The slag was frothy, full of gas, and porous after cooling, when it was low in manganese. This was observed particularly during period 1 (table 79). The high-alumina slags were dense, indicating that reduction of manganous oxide and gas formation were less active.

The numerous variables that affect the operation of a blast furnace often make it difficult to draw conclusions from operating data. In this particular case operation on high-alumina charge was sufficiently different from the operation on the high-silica charge to leave little doubt as to a difference in smelting characteristics of the two materials. The rather sharp increase in the percentage of manganese in the slag when the high-alumina charge reached the crucible is shown in table 80, which contains analyses of the last slag produced during period 3 and the first flushes of period 4. There was very little change in tuyère temperature during the 48-hour period. In fact, the tuyère temperatures were uniformly high throughout the entire test. The amount of burden was held constant. Blast temperature were somewhat lower during the operation on high-alumina charges, but in view of the comparative small difference in tuyère temperatures the difference in blast temperatures does not explain the large difference in the operation on the two types of material. The capacity of the crucible below the tuyères was materially decreased when operating on the high-alumina charge. This was due to the incrustation of slag on the bottom and sides of the crucible.

TABLE 80. - Slag Analyses, Showing Transition from Normal to High-Alumina Slag, Percent

Samples taken 24 hours before high-alumina charge reached crucible

Percent				
Mn	SiO_2	Al_2O_3	CaO	MgO
12.88	27.7	11.2	33.0	9.40
15.9	24.8	11.1	28.2	9.70
15.3	22.6	10.8	30.25	12.31
17.4	23.02	10.7	30.2	12.20

Samples taken 24 hours after high-alumina charge reached crucible

22.3	26.16	11.38	18.5	9.11
26.8	20.00	13.00	14.2	7.06
25.7	19.32	17.3	17.2	7.03
26.4	18.7	17.7	19.7	6.95

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As a result, the slag appeared in front of the tuyères in a comparatively short time after cast. This decrease in the volume of slag which could be held in the crucible below the tuyère level, where a highly-reducing atmosphere prevailed, aggravated the difficulty of being able to reduce the manganous oxide from the high-alumina slags.

Effect of Slag Basicity and Magnesia on Recovery of Manganese from High-Alumina Slags

The first step in the method proposed to produce ferromanganese from manganiferous iron ores consisted in smelting a charge of such ore in the experimental blast furnace. During this test, the alumina in the slag ranged from 9.4 to 21 percent. At that time an effort was made to determine the effect of alumina on the completeness with which manganous oxide was reduced from the slag. The conclusion reached was that as the alumina in the slag increased the use of additional bases had less effect in decreasing the manganese in the slag; that is, there was a greater decrease in the manganese in the slag for a given increase in basicity when the alumina averaged about 10 percent than when it varied up to 20 percent. This same tendency was more pronounced during the production of ferromanganese from high-alumina charges. The alumina in the slag made during the production of high-phosphorus spiegel was almost as high as it was in the slag made during the ferromanganese test. There was, however, a large difference in the relative percentage of silica and alumina in the slag made in the two operations. The spiegel-slag contained from 2 to 2.5 times as much silica as alumina, whereas the ferro-slag contained approximately equal amounts of these two oxides.

In attempting to reduce the manganous oxide in the slag during the ferromanganese test, the basicity was varied from 1.22 to 1.65. As shown in table 81, the manganese in the slag was practically the same when the basicity was 1.22 and 1.65. During the 10 days operation on high-alumina slag there was rarely less than 20 percent of manganese in the slag. The burden throughout this period was the same as during period 1, when the manganese in the slag averaged 11.5 percent.

Increasing the amount of magnesia in the slag was more effective than increasing the basicity in aiding the reduction of manganous oxide from the slag. For example, in table 81 a definite relation exists between the magnesium oxide in the slag and the percentage of manganese.

TABLE 81. - Average Slag Analyses Showing Effect of MgO on Percentage of Manganese

Group	Percent					Basicity
	Mn	MgO	CaO	SiO_2	Al_2O_3	$\frac{CaO + MgO}{SiO_2}$
1	19.2	11.0	21.3	20.2	17.35	1.59
2	24.4	7.9	20.6	18.2	17.20	1.65
3	24.2	6.2	19.0	20.7	17.70	1.22
4	26.5	5.9	20.5	18.3	17.20	1.45
5	28.4	2.7	21.4	15.7	16.20	1.53

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The percentage of manganese in the slag, however, was about the same when the basicity was 1.63 in group 2 as it was when the basicity was 1.22 in group 3. McCaffery, Cesterle, and Fritsche (248) have studied the effect of magnesium oxide upon the viscosity of the quarternary system $CaO \cdot SiO_2 \cdot Al_2O_3 \cdot MgO$. Their results show that magnesia has a pronounced effect towards increased fluidity of silica-alumina-lime-magnesia slags. The slags produced in the experimental furnace on high-alumina charges contained 25 to 35 percent manganous oxide. Such large percentages of a fifth constituent leave some doubt about applying viscosity measurements made on a four-component system. It appears probable that the higher percentages of magnesia did aid reduction of manganous oxide by decreasing the viscosity of the slag. The amount of trapped shot in the slag as indicated by the total iron determinations was less with higher percentages of magnesia. This indicates magnesia had a thinning action on the slag. Magnesia, however, was more of a palliative than a cure for the troubles encountered with high-alumina slag.

Operation of Experimental Blast Furnace on Manganese Ores

The experimental furnace was operated for a short time on two manganese ores. Ore 2 was high in alumina and the other contained silica and alumina in normal proportions (see p. 238). The time available was too short to correct channeling of the gas, which was particularly bad on ore 1. The analysis of metal produced from manganese ore is given in table 82.

Commercial furnaces, which have a comparatively large amount of reserve heat in the hearth or crucible, are much less sensitive to changes and irregularities than the small furnace. Nonuniformity in size of raw materials and the inevitable nonuniformity in gas distribution, however, tend toward inefficient operation in large furnaces.

Temperature surveys were made across several planes of the experimental blast furnace to obtain a comparison in gas distribution when operating on the high-manganese slag and when operating on natural ores. Figure 33 shows the position of the test holes. The observations are reported in table 83 and in figure 34. All observations made across various planes when the furnace was operating on high-manganese slag showed uniform increases in temperature from the inwall toward the center of the furnace.

Temperature measurements made through hole 64 in plane 6 on June 4 were very similar to those made through the same hole on June 9. A striking change is shown between the gradual temperature changes on these days and the sharp fluctuation of temperatures with distance from the inwall when the furnace was filled with fine ore. The physical characteristics of the slag or artificial ore were important enough in the operation of the small furnace to offset the advantages of lower silica in the natural ores. This would probably not be true of a large furnace. The physical structure of the slag, which resembles sinter, would, however, offer an advantage in establishing uniform distribution of the gas, which is essential to uniform preparation of the material in the upper part of the furnace.

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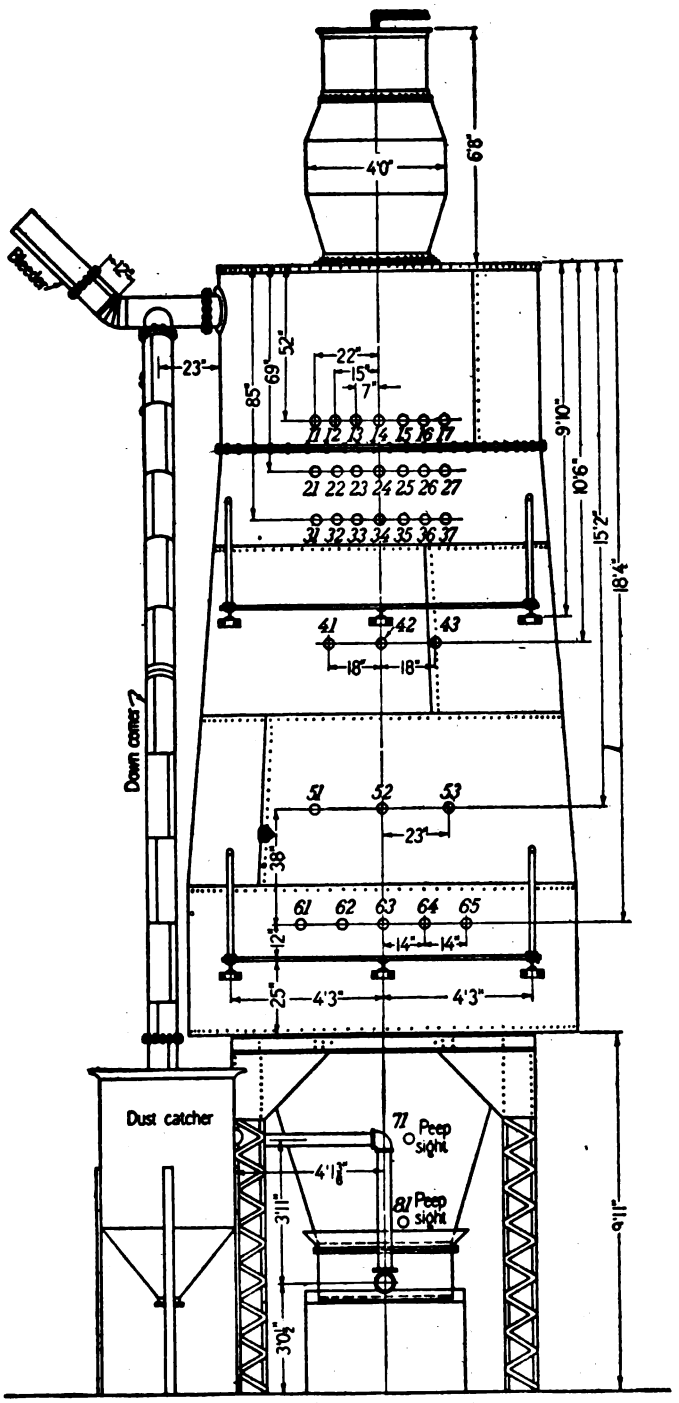

Figure 33.- Position of holes in lining of experimental furnace.

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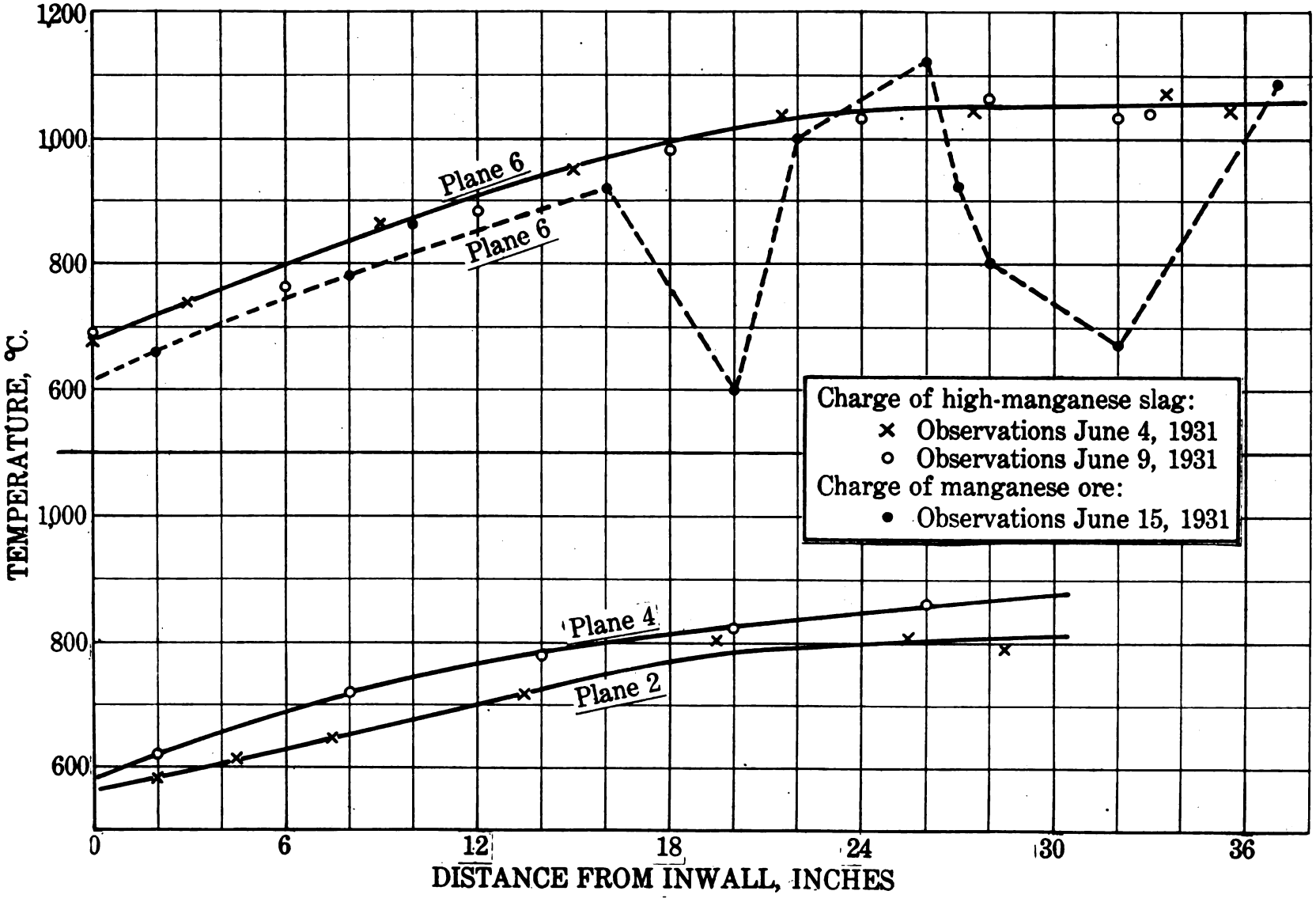

Figure 34.- Temperatures along three planes of experimental blast furnaces.

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The short period of operation on natural ores was significant in one other respect. Ore 2 was used first, being followed with a charge of ore 1, which was finer and apparently settled through the furnace more rapidly. About 4 percent more manganese was recovered in the slag and metal than was charged in ore 2, indicating that substantial amounts of ore 1 had worked down through the furnace at a rate more rapid than the normal rate of stock descent. A manganese balance for the period of operation on ore 1 showed a stack loss of 31.8 percent. Considering the entire period on natural ores, the stack loss averaged 27.8 percent compared to an average stack loss of about 4 percent for operation on high-manganese slag. Such a large difference in stack loss would not probably be found if the two types of material were smelted in large furnaces. The data, however, from the small furnace indicate that much of the so-called stack loss is a dust loss which may vary widely with the ore used. The physical structure of high-manganese slag would practically eliminate this dust loss.

TABLE 82. - Analyses of Ferromanganese Made from Manganese Ore, Percent

Cast no.	Manganese	Phosphorus	Silicon
203	79.7	0.43	0.05
204	76.9	----	----
205	80.1	.40	----
206	76.4	----	.26
207	78.7	.34	----
208	79.3	----	----
209	75.4	.40	.10
210	76.6	----	----
211	76.6	.34	----
212	78.0	----	.08
213	76.6	.42	----
214	75.8	----	.59
215	73.01	.43	----
216	79.46	----	.02
217	76.10	.47	----
218	80.10	----	.02
219	75.8	.39	----
220	77.7	----	.06
221	76.6	.41	----
222	73.8	----	.36
223	78.0	----	.39

Summary of Experiments on Production of Ferromanganese from Manganiferous Iron Ores

The importance of manganese in the production of steel and the comparatively small domestic reserves of manganese ores have focused attention upon the problem of producing ferromanganese from our more abundant deposits of manganiferous iron ores. The experimental work was centered upon the brown manganiferous iron ores which occur in large well-developed deposits on the Cuyuna range in Minnesota.

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TABLE 83. - Temperatures Across Three Planes of Experimental Blast Furnace During Ferromanganese Test

Distance from inwall, inches	Temperature, °C.
Hole 23, June 4, 1931	
2.0	585
4.5	615
7.5	650
13.5	720
19.5	805
25.5	810
28.5	790
Hole 43, June 9, 1931	
2.0	620
8.0	720
14.0	780
20.0	820
26.0	860
Hole 64, June 4, 1931	
0.0	685
3.0	740
9.0	865
15.0	950
21.5	1,035
27.5	1,040
33.5	1,070
35.5	1,042
Hole 64, June 9, 1931	
0.0	690
6.0	760
12.0	880
18.0	980
24.0	1,030
30.0	1,060
34.0	1,030
35.0	1,035
Hole 64, June 15, 1931	
2.0	660
8.0	780
10.0	860
16.0	920
20.0	600
22.0	1,000
26.0	1,120
27.0	920
28.0	800
32.0	670
37.0	1,085

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Tests with an experimental blast furnace, a small open-hearth furnace, and small electric furnaces of the arc type have demonstrated that ferromanganese can be produced from manganiferous iron ores by a three-step process, as follows:

1. The ores are smelted in a blast furnace according to the general practice of producing spiegeleisen. The metal produced does not, however, conform to standard grades of spiegel. It would contain from 12 to 15 percent manganese, 0.5 percent phosphorus, and about 80 percent iron. There is no market for metal containing manganese, iron, and phosphorus in these proportions.

2. High-phosphorus spiegel, made in step 1, is next treated in either a basic open-hearth furnace or a basic electric furnace. Iron ore is added to oxidize the manganese and to get it into the slag. To do this rapidly and with the desired degree of completeness an excess of iron ore is used. Phosphorus is oxidized simultaneously with the manganese and enters the slag. There is enough difference in the rate of reduction of ferrous phosphate, ferrous oxide, and manganous oxide to permit adjusting the iron and phosphorus with a comparatively small return of manganese to metal. The necessary reducing conditions can be established by covering the slag with a 2- or 3-inch layer of small coke. When the slag contains 25 to 35 percent ferrous oxide it is very fluid, but as the ferrous oxide content is lowered to 6 or 8 percent and the manganous oxide is increased to 60 to 70 percent the slag becomes very viscous unless silica or alumina is added as a thinning agent. It would be feasible to add predetermined amounts of these oxides at the beginning of the heat or to use iron ore containing amounts of silica and alumina needed to obtain a workable slag. Although alumina has a thinning effect upon the slags, it is neither as abundant nor as cheap as silica. If some substantial advantage could be gained in the next operation of converting the high-manganese slag or artificial manganese ore into ferromanganese, the use of alumina might be justified.

The electric furnace has distinct metallurgical advantages over the open-hearth furnace for separating the manganese from the iron and phosphorus in low-grade spiegel. The chief advantages are in flexibility and in a more strongly reducing atmosphere which permit greater speed in adjusting the iron and phosphorus to the limits usually set for manganese ore.

3. High-manganese slag containing 60 to 70 percent manganous oxide, 5 to 6 percent ferrous oxide, and about 20 percent silica plus alumina resembles sinter, another fused product. It is porous and contains manganosite as a principal slag constituent. There was no serious doubt about being able to produce ferromanganese from high-manganese slag, but there was evidence from crucible tests indicating that alumina has distinct advantages over silica as a thinning agent. It was desirable to check this evidence with an experimental furnace test. Information obtained upon this point and upon other phases of ferromanganese practice follows:

(a) Operation of the experimental blast furnace on high-manganese slags fluxed entirely with silica was more satisfactory than on slags fluxed with alumina. In view of the greater cost of alumina as compared to silica and of the results obtained in smelting the two types of slag in the experimental furnace, alumina is not recommended as a thinning agent for high-manganese slag intended for use in the production of ferromanganese.

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(b) High-manganese slag resembles sinter in physical texture. It is porous, contains little potential dust, and undergoes no size degradation in the furnace. Dust losses were almost completely eliminated in operating the experimental furnace on this material. The total loss of manganese due to dusting of the ore, volatilization of manganese, and oxidation of the manganese at the tuyeres followed by dusting ranges from 15 to 25 percent in practice. Some manganese ores result in high stack losses because they become very soft after heating and break down to dust under the abrasive and crushing action of the coke in the blast furnace. Size degradation in the furnace not only leads to dust losses but causes channelling of the gases. The gas distribution in the experimental furnace was far more regular when operating on the high-manganese slag than when operating on two natural manganese ores, one of which was particularly susceptible to dusting. Due to the small amount of dust produced when operating the experimental furnace on high-manganese slag, it was possible to isolate the loss of manganese by volatilization. This loss, not distinguishable from ordinary dust losses in commercial practice, averaged 4 percent of the manganese charged. The physical character of the slag, which was particularly beneficial in operating the small furnace, would also be desirable in the operation of industrial furnaces.

(c) High-manganese slags are less desirable chemically than the imported ores from which most of our ferromanganese is produced. Silica, essential in the second step in maintaining a fluid and workable slag in the presence of 60 to 70 percent manganous oxide, would increase the weight of slag per ton of ferromanganese about 1,000 pounds over the amount normally produced. This additional slag would, if it contained 10 percent manganese, represent a loss of about 5 percent of the manganese charged. Such a loss would probably be offset by eliminating dust losses. The 1,000 pounds of additional slag would require additional coke and would decrease furnace output.

(d) Results from the experimental furnace indicate that it is desirable to use part dolomite as flux. This is particularly true as the amount of basic fluxes is increased. Slag reaching the tuyeres and crucible contain manganous oxide which together with calcium oxide and magnesium oxide -- essential in the final stages of reduction -- tends to increase the viscosity of the slag. It appears that magnesium oxide promotes fluidity and is particularly valuable, while the slag is still high in manganous oxide. Equal amounts of dolomite and calcite gave the best results on the experimental blast furnace.

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